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ELEKTROLUMINESTSENTS-SEADMETES KASUTATAVATE MATERJALIDE KASVATAMINE JA UURIMINE

GROWTH AND CHARACTERIZARIZATION OF MATERIALS FOR ELECTROLUMINESCENCE DEVICES

Proceedings on Electroluminescence

XIX



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CONTENTS

J.Aarik, A.Aidla, A.Jaek, AA.Kiisler
On the mechanism of atomic layer deposition of aluminium oxide films
J.Aatik, A.Jaek, AA.Kiisler, V.Sammelselg
Composition of oxide films grown by ALE from AlCl ₃ and H ₂ O
J.Aarik, A.Aidla, A.Jaek, AA.Kiisler
Time delays in flow-type atomic layer epitaxy reactor
J.Friedenthal, H.Koppel, T.Uustare
AP-MOCVD layer growth of ZnO in the H_2 -Zn(C_2H_5) ₂ -CO ₂ system
V Seeman, J. Pung, M Danilkin, M Kerikmäe. 37
V_centres in plastically deformed CaS
v-centes in plastically deformed Cas
H.Siimon, T.Uustare, J.Lembra
ALE model considering the surface structure of the growing binary compound
U Siimon T Uustare I Lembra 55
Minimion, 1. Oustate, J. Lemota
Kinetics of cyclic deposition of a binary compound
J.Aarik, H.Siimon
Growth rate and source material utilization efficiency in MBE under conventional and
ALE conditions
I Rammo, I Kaasik, M Lenist, I. Matisen, A – A Tammik, F. Vilt. 60
Investigation of SrS_Ce photoluminescence excited by short pulses
investigation of 515-cc photoruminescence excited by short pulses.

ON THE MECHANISM OF ATOMIC LAYER DEPOSITION OF ALUMINIUM OXIDE FILMS

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Abstract

Using data concerning the time delays of reagent pulses and the behaviour of film mass deposited during ALE cycle some models of film formation from $AlCl_3$ and H_2O are discussed. It is shown that the growth mechanism is very sensitive to the substrate temperature and every model proposed is valid only in narrow temperature range.

Introduction

Atomic layer epitaxy (ALE) is widely used for the deposition of Al_2O_3 films with different pairs of source materials employed. $AlCl_3 - H_2O$ [1-3], $AlCl_3 - O_2$ [4-6], $AlCl_3 - 2$ -methyl-2-propanol [7-8], $Al(CH_3)_3 - H_2O$ [9] and $Al(CH_3)_3 - H_2O_2$ [10] are the systems used in ALE. A number of models has been proposed for describing the growth process. Even in the case of the systems where $AlCl_3$ has been used as Al source different growth mechanisms have been considered.

Oya et al. [4–6] have established that decomposition of adsorbed AlCl₃ plays an important role in formation of Al₂O₃ films from AlCl₃ and O₂ at temperatures 600–800°C. Leskelä et al. [8] have supposed that in the AlCl₃ – 2-methyl-2-propanol system the reaction goes via aluminium hydroxide. In our previous study [3] we have shown that different ways for the formation of Al₂O₃ from AlCl₃ and H₂O are possible while the growth mechanism depends on the substrate temperature. We have found that at high temperatures (T>300°C) AlCl₃ adsorbs without exchange reaction and the limits to the growth rate are very similar to those described by Oya and Sawada [6]. At low temperatures hydroxyl groups take an active part in the exchange reactions. Thus, in this case the situation is similar to that observed by Leskelä et al. [8].

However, the reality is even more complicated because AlO(OH) and Al(OH)₃ can also be formed. The presence of OH groups has been determined by IR spectroscopy in the films grown using AlCl₃ – 2-methyl-2-propanol [8]. It has been also shown that the density of Al atoms in films grown at temperatures below 190°C using AlCl₃ and H₂O corresponds to that calculated for AlO(OH) [11]. At the same time the dependence of Al to O ratio on temperature indicates that Al₂O₃ and AlO(OH) should be present in the films simultaneously. Consequently our previous models should be analysed anew, taking into consideration the possibility of formation of AlO(OH) as well as Al₂O₃.

In this paper we present some additional data which give an opportunity to develop our understanding of surface reactions between $AlCl_3$ and H_2O . A new technique – the measurement of time delays of reagent pulses [12] has been used in our studies.

Experimental

Experiments were carried out in low pressure flow-type ALE reactor in the temperature range of 50-340°C. AlCl₃ and H₂O were injected into the reactor alternatively using solenoid valves. The valves were operated by personal computer "Tartu". The reagent pulse fluxes were controlled by adjusting the flows of carrier gas and the temperature of AlCl₃ and H₂O cells. Temperature of the reaction chamber and AlCl₃ cell was stabilized with the accuracy of $\pm 0.3^{\circ}$ C.

The behaviour of the film mass during ALE cycle was measured with time resolution of 1 s using quartz microbalance [3]. To get information about transient processes we used relatively small flux intensities of reagent flows.

Advantageous information was obtained from time delay measurements using slit adsorber between gas inlet and mass sensor. The length of the adsorber was chosen equal to 50 mm. Details of the technique and adsorber design have been described elsewhere [12].

Results

An unexpected phenomenon observed in this study was the saturation of adsorption at temperatures as low as 50°C. Moreover the level Δm_1 at which the adsorption saturated during exposition to AlCl₃ flow did not depend on the AlCl₃ pressure even if that was varied more than an order of magnitude. At the same time Δm_1 considerably depends on the reactor temperature T_R.

Fig.1 shows variations of the resonant frequency of mass sensor $\Delta f_1 = A\Delta m_1$, where A is a constant describing the sensitivity of mass sensor. A minimum at 100°C and a maximum at 200°C are clearly observable on the experimental curve while obvious increase of Δf_1 becomes evident at temperatures below 100°C. The latter is the steeper the longer purge time is used before the AlCl₃ pulse. Similarly the ratio $\Delta m_1/\Delta m_0$, where Δm_0 is the increment of film mass during complete ALE cycle, decreases down to 1.0 with the decrease of temperature when long purge time has been used before the AlCl₃ pulse (Fig.2). At purge times below 25s $\Delta m_1/\Delta m_0$ is nearly constant in the range of 50-200°C. It should be noted that at temperatures 100-350°C the data for $\Delta m_1/\Delta m_0$ obtained in this study coincide with those published earlier [3].

Fig.3 shows delay times of AlCl₃ pulses as a function of temperature of an adsorber placed between reagent gas inlets and mass sensor. The behaviour of experimental data resembles that shown in Fig.1. The most essential difference is that the former is much more expressive than the latter.



Fig.1. Resonant frequency decrease of quartz microbalance during exposition to AlCl₃ flow as a function of growth temperature at different purge times before AlCl₃ pulse.



Fig.2. Ratio of the mass increase caused by adsorption of AlCl₃ to the mass increase during complete ALE cycle as a function of growth temperature at different purge times before AlCl₃ pulse.

We established that in the case of high H_2O doses and short purge times the delays are very sensitive to the duration of purge time. This effect seems to be due to the incomplete evacuation of H_2O from the reactor. Therefore most of the experiments were performed using low H_2O doses and purge times of 15-300s before injection of AlCl₃.

It can be shown that delay times t_d plotted in Fig.3 are proportional to the number of particles adsorbed per unit area [12]. Taking into consideration that the values of Δf_1 presented in Fig.1 are proportional to the mass increases per unit area, we can calculate the relative mass increase per adsorbed AlCl₃ molecule. Fig.4 shows this quantity as a function of substrate temperature. Unfortunately similar dependence could not be correctly calculated in the case of adsorption of H₂O because the respective mass increments are considerably smaller. Correspondingly the relative errors of recording Δf and t_d increase, making their ratio inadequate.

Discussion

Determination of $\Delta m_1/\Delta m_0$ as well as density and relative mass of adsorbed particles enables us to deduce surface reactions taking place during adsorption of AlCl₃. It was established previously that AlCl₃ adsorbs without exchange reactions at



Fig.3. Time delay of AlCl3 pulse as a function of adsorber temperature.



Fig.4. Relative mass increase per a chemisorbed particle as a function of growth temperature.

temperatures above 300°C [3]. Indeed, comparing the experimental values of $\Delta m_1/\Delta m_0$ (Fig.3) with different models describing formation of Al₂O₃ as well as AlO(OH) and Al(OH)₃, one can be convinced that the surface reactions which can be fitted with the data at T>300°C can be expressed as:

$$2nO^{2-}(ad) + 2AlCl_{3}(g) \rightarrow 2(nO^{2-}AlCl_{3})(ad),$$
(1)
$$2(nO^{2-}AlCl_{3})(ad) + 3H_{2}O \rightarrow 3O^{2-}Al_{2}O_{3}(ad) + (2n-3)O^{2-}(ad) + 6HCl(g) (2)$$

In Eq.1-2 n is the number of oxygen sites covered by one adsorbed chloride molecule.

Taking into account that ion radius of Cl⁻ is equal to 1.81Å and that of O^{2-} is equal to 1.36Å it can be estimated that n=6. Correspondingly the ratio of the coefficients in the first terms of the left side of Eq.1 and right side of Eq.2 determining the maximum oxygen monolayer coverage per ALE cycle equals to 0.25. Considering that the oxygen monolayer spacing for hexagonally close-packed sapphire is 2.17Å the maximum growth rate should be 0.54Å per cycle. This value is close to the experimental value obtained at 350-470°C [3]. Eq.1-2 indicate also that some oxygen sites covered by AlCl₃ during the first step can be vacated again during the next one.

At lower temperatures $\Delta m_1/\Delta m_0$ curve does not give any authentic proof of growth mechanism. Provided that Al₂O₃ is the final product of reactions the surface

reactions can be described as [3]

$$\begin{aligned} & 2n(OH)^{-}(ad) + 2AlCl_{3}(g) \rightarrow ((2n-3)(OH)^{-}+3O^{-}) \cdot Al_{2}Cl_{3}(ad) + 3HCl(g), \quad (3) \\ & ((2n-3)(OH)^{-}+3O^{-}) \cdot Al_{2}Cl_{3}(ad) + 3H_{2}O(g) \rightarrow \\ & \rightarrow 3O^{-} \cdot Al_{2}(OH)_{3}(ad) + (2n-3)(OH)^{-}(ad) + 3HCl(g). \end{aligned}$$

In Eq.3-4 n=3, while the maximum oxygen monolayer coverage and growth rate per ALE cycle equal to 0.5 and 1.08 Å, respectively. $\Delta m_1/\Delta m_0$ equals to 1.54 and is in good agreement with our data at T_R=100-180°C.

However, taking into account that AlO(OH) and $Al(OH)_3$ as well as Al_2O_3 can be formed, some additional models must be considered. It can be shown that in the case of reaction sequencies

$$n(OH)^{-}(ad) + AlCl_{3}(g) \rightarrow n(OH)^{-} \cdot AlCl_{3}(ad) , \qquad (5)$$

$$n(OH)^{-} \cdot AlCl_{3}(ad) + H_{2}O(g) \rightarrow$$

$$\rightarrow 3(OH)^{-} Al(OH)_{3}(ad) + (n-3)(OH)^{-}(ad) + 3HCl(g)$$
(6)

and

$$n(OH)^{-}(ad)+AlCl_{3}(g) \rightarrow (n-1)(OH)^{-}O^{-}AlCl_{2}(ad)+HCl(g),$$
(7)
(n-1)(OH)^{-}O^{-}AlCl_{2}(ad) + H_{2}O(g) \rightarrow

$$\rightarrow (OH)^{-} O^{-} Al(OH)_{2}(ad) + (n-2)(OH)^{-}(ad) + HCl(g)$$
(8)

the values of $\Delta m_1/\Delta m_0$ equal to 1.71 and 1.59, respectively, also coincide with the experimental curve satisfactorily in the same temperature range. Consequently additional data have to be used for selecting any of these models. In Eq.5-6 n=6. The maximum growth rate is 0.5 monolayers per cycle. In the case of Eq.7-8 these values are equal to 4 and 0.5 respectively. As one can see the last three models do not differ in growth rate. However, the area occupied by an adsorbed chloride molecule as well as the mass exchange per an adsorbed particle differ significantly.

Using the data presented in Fig.4 and assuming that adsorbate consists of AlCl₃ at temperatures above 300°C one can calculate the composition of adsorbate AlCl_x at low temperatures. These calculations show that x equals to 1.5 ± 0.5 , 1.8 ± 0.6 and 1.1 ± 0.4 at temperatures 200, 120 and 60°C respectively. Therefore the surface reactions cannot be expected to go on according to Eq.5–6. Unfortunately dispersion of experimental data does not allow us to determine the contribution of the reactions described by Eq.3–4 and those described by Eq.7–8. However, obtained values of x indicate that the role of reactions described by Eq.7–8 should increase at temperatures below 200°C resulting in increase the content of OH–groups and thus oxygen to aluminium ratio. This conclusion is in good agreement with the data of x–ray micro–analysis [11].

At temperatures below 100°C the surface density of AlCl₃ adsorbed per ALE cycle increases abruptly indicating the possibility of multilayer adsorption. Similar behaviour of ALE growth rate of TiO₂ observed by Aleskovskii and Drozd [13] at the same temperature range, has been explained by adsorption of molecular H₂O on the

3

surface covered by OH groups. It is interesting to note that in our case this explanation seems to be true as well. Indeed, we established that the adsorbate formed during exposition of the surface to AlCl₃ at 60°C consists of AlCl_{1.1}. Consequently the exchange reactions taking place during chloride adsorption are more complete than those predicted by Eq.3, 5 and 7.

Provided that the surface is covered by an OH monolayer and an overlaying H_2O monolayer the impinging AlCl₃ should at first react with H_2O giving most probably a monolayer of AlO(OH) or Al(OH)₃ and releasing HCl. Further, during the same exposition step AlCl₃ interacts with the just-formed AlO(OH) or Al(OH)₃ layer giving an additional AlCl_x monolayer adsorbed on the solid surface and releasing HCl again. According to this scheme the first monolayer does not contain chlorine. Therefore the mean value of x for the double layer is significantly lower than that predicted by Eq.3, 5 and 7.

During the following exposition step impinging H_2O reacts with AlCl_x releasing HCl and covering the surface with OH groups and further, provided that the interaction time is long enough, forms a monolayer of molecular water on OH groups.

Unfortunately the lack of experimental data concerning the kinetics of H₂O adsorption does not allow us to describe these processes more precisely. Thus for development of the growth model corresponding studies at low growth temperatures are of great interest.

Conclusions

Using the time delays of reagent pulses and the mass of adsorbate deposited during ALE cycle the mass exchange per an adsorbed particle as a function of substrate temperature has been estimated. This relationship together with the data concerning the growth rate enables us to conclude that a significant fraction of OH groups should remain in the films grown at temperatures below 200°C. At the same time they confirm that Al(OH)₃ does not form at temperatures as low as 100°C

Our data also indicate that at temperatures below 100° C a monolayer of molecular H₂O adsorbed on the surface covered by OH groups should play an important role in the surface reactions.

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COMPOSITION OF OXIDE FILMS GROWN BY ALE FROM AICI3 AND H2O

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Abstract

The composition of aluminium oxide films grown by ALE using AlCl₃ and H₂O as the source materials has been investigated. It has been shown that the films grown at low temperatures contain significant amount of hydroxyl groups and chlorine. The films grown at temperatures above 470°C have Al to O ratio corresponding to that of Al₂O₃ and chlorine content below 0.5 mass per cent.

Introduction

Recently the growth of aluminium oxide thin films by atomic laver epitaxy (ALE) and the characteristics of these films have been studied in several papers [1–8]. Various source materials and wide range of growth temperatures have been used in these experiments Among the source materials AlCl₃ and H₂O form a pair most frequently used for the ALE-growth of aluminium oxide films. Unfortunately the properties of these films strongly depend on the growth temperature [8]. It has been shown that the growth mechanism also depends on substrate temperature [8].

Hiltunen et al. [7] have studied the composition of aluminium oxide films grown by ALE at temperatures ranging from 250 to 500°C. They have shown that, in the case of AICl₃ as the aluminium source and H₂O or various alcohols as the oxygen source, the films contain some amount of residual OH–groups and chlorine. However, there are no quantitative data about the aluminium to oxygen ratio. Moreover, the data concerning the composition of the films grown at temperatures below 250°C are absent at all. At the same time there exists a great variety of applications which prescribe low deposition temperatures. Thus the study of the composition of such films is of significant importance.

in this paper we investigate the composition and structure of tilns grown by ALE at temperatures of 90–760°C using AlC(3 and H₂O as the source materials

Experimental

The films were grown on the slides of glass and fused quartz as well as on silicon and sapphire substrates using low-pressure gas-transport reactor. The details of film growing have been described earlier [8]. The ALE cycle used in our experiments includes the injection of AlCl₃, the first purge time, the injection of H₂O and the second purge time with durations 1, 0.5, 0.2 and 1.3-4.3 s respectively.

The thickness of the grown films was calculated from the spectral oscillations of optical absorption [8]. The structure of the films was studied by high energy electron diffraction. The composition was measured using X-ray microanalysis and the spectrometric method for quantitative chemical analysis developed by Gentry and Sherrington [9].

In the last method the films were dissolved in KOH or hydrochloric acid. Aluminium was trapped using 8-hydroxyquinoline. Aluminium-8-hydroxyquinolate was extracted with trichloromethane and optical transparence of obtained solution was measured using spectrophotometer "Specord M40" (Carl Zeiss Jena). The mass of Al in the films was found by comparing the transparence of the solution with that of reference solutions. This method enabled us to determine Al content with the accuracy better than $\pm 1\mu g$. Oxygen mass fraction was determined using X-ray microanalysis, considering the data of chemical analysis of Al as a reference.

Results and discussion

High energy electron diffraction measurements indicate that the films grown at temperatures $270-500^{\circ}$ C are amorphous. The films grown on silicon substrates at 600-760°C have some polycrystalline inclusions while single-crystal films grow on α -Al₂O₃ substrates at 600-760°C.

Using the values of Al content and optically determined thickness of the films we calculated the density of Al atoms in the films. As one can presume this quantity increases with the increase of growth temperature (Fig.1). Proceeding from the published data on the density for bulk material we obtained the density of Al atoms equal to $(1.85-1.95)\cdot10^{22}$, $(3.02-3.45)\cdot10^{22}$ and $4.69\cdot10^{22}$ cm⁻³ for different crystal modifications of Al(OH)₃, AlO(OH) and Al₂O₃ respectively [10]. Comparing these quantities with the data presented in Fig.1 one can be convinced that the films grown at temperatures above 350° C should contain mostly Al₂O₃. It must be noted that even in the case of films grown at temperatures as low as 100° C the density of Al atoms significantly exceeds the values calculated for the bulk Al(OH)₃.

Electronprobe measurements show that oxygen to aluminium mass ratio increases with the decrease of the growth temperature (Fig.2). In case of the films grown at temperatures as low as 90-100°C this ratio exceeds that of Al_2O_3 by a factor of 1.12 only. At the same time a noticeable increase of Cl content was observed (Fig.3) Therefore besides Al_2O_3 and AlO(OH) the films should contain some AlOCl. Thus a: low substrate temperatures the exchange reactions are not complete in the case of the exposition times used in this study. Rough estimation shows that Cl weight fraction equal to 0.085 corresponds to the oxygen to chlorine mole ratio of 12. From these data it can be calculated that the mole fraction of AlOCl is 14 per cent and about 30 per cent of oxygen atoms occur as constituent parts of OH groups in the films grown at 100°C. For the films grown at 270°C these values are 3 and 14 per cent respectively.

Fig.4 shows the surface density of Al atoms deposited during an ALE cycle as a function of growth temperature. The experimental curve has a maximum at $T=300^{\circ}$ C. It is interesting to note that this value does not coincide with the temperature corresponding to the maximum of surface density of adsorbed chloride estimated from the time delays of the reagent pulses [11]. Most probably the difference is caused by the difference in the purge times preceding the AlCl₃ pulses.



Fig.1. Volume density of alumunium atoms as a function of growth temperature.



Fig.2. Oxygen to aluminium mass ratio as a function of growth temperature.



Fig.3. Chlorine mass fraction as a function of growth temperature.

Indeed, the purge times in time delay measurements (15-300s) sufficiently exceed those used in this study. Approximating our previous data [12] with two curves corresponding to various purge times (Fig.5) it becomes evident that the temperature range where the growth mechanism changes does depend on the purge time. At shorter purge times the increase of $\Delta m_1/\Delta m_0$ indicating the change of growth mechanism begins at higher temperatures. This behaviour can be expected because the increase of $\Delta m_1/\Delta m_0$ has been explained as the result of dissociation and/or desorption of OH groups.



Fig.4. Surface density of aluminium atoms deposited during an ALE cycle as a function of growth temperature.

The comparison of the surface density of Al atoms deposited during an ALF cycle with that in a completely filled monolayer demonstrates that more than one ALE cycle is needed to formate an oxide monolayer. Taking into account that the ionic radius of O^{2-} is 0.136nm [13] one can find that the surface density of oxygen in a close-packed monolayer is 1,56 10^{15} cm⁻² At the same time the data presented in Fig.4 do not reach this value.

Thus the density of Al in the adsorbate seems to be limited by steric effects rather than by the density of Al sites. The most important role in this limit plays the size of chlorine ions. Using ionic radius of Cl⁻ equal to 0.181nm [13] one can find that the maximum surface density of chlorines in a plane monotayer is $8.81 \times 10^{14} \text{ cm}^{-2}$. This

value is approximately 3 times higher than the surface density of Al atoms deposited during an ALE cycle at temperatures above 400°C. Therefore every Al atom can be accompanied by 3 chlorines located in a single monolayer. Of course we have no assurance that chlorine ions form a plane close-packed monolayer. Thus these speculations can not be used for making conclusions about the surface reactions.



Fig.5. Ratio of the mass increase caused by adsorption of AlCl₃ to the mass increase during complete ALE cycle as a function of growth temperature [12]. The curves correspond to different purge times after H_2O pulses.

At the same time we can estimate the density of oxygen and chlorine ions in the grown film. The data concerning aluminium to oxygen mass ratio and the surface density of Al enable us to establish that the surface density of O^{2-} deposited during one ALE cycle has also maximum at T=300°C. However, the area covered by oxygen and chlorine ions together has no such maximum. The calculations show that the surface coverage by oxygen and residual chlorine is 0.40, 0.39 and 0.26 at 100, 270 and 470°C respectively.

The area occupied by one chlorine and oxygen ion has been taken equal to 0.113 and 0.064 nm^2 , respectively, in the calculations. These values correspond to the closest packing of ions.



Fig.6. Growth rate as a function of temperature.

Similarly one can calculate the volume occupied by Cl⁻and O²⁻ deposited during complete ALE cycle. This quantity describes the contribution of ionic volume to the increase of film thickness per cycle. Our calculations show that the thickness increase due to the volume of oxygen and chlorine ions is 0.069, 0.066 and 0.043 nm at 100, 270 and 470°C respectively. Comparison of these data with the growth rate obtained from independent measurements (Fig.6) shows that the relative contribution of the volume of anions to the thickness increment per one ALE cycle is 0.56, 0.66 and 0.74 at 100, 270 and 470°C respectively. The last value coincides very well with the theoretical limit corresponding to the closest packing. It is surprising that the packing density of this amorphous film is so close to that of monocrystal. Partly this can be due to our experimental error which can reach \pm 10 per cent. However, very low etching rates and high refractive indexes [8] also indicate that the density of the films does have high values.

It is interesting to note that the decrease of packing density at low growth temperatures is accompanied with the increase of surface roughness clearly observeable by scanning electron microscopy. Unfortunately all the reasons for this behaviour are not clear. Rough estimations show that the presence of OH groups in the films instead of O^{2-} has an effect which does not exceed 25 per cent of that observed in our experiments. Therefore the decrease of the surface migration velocity and blocking of more than a single Al site by every residual chlorine have to be considered as other reasons for the decrease of packing density.

Conclusions

The composition of oxide films grown by ALE from AlCl₃ and H₂O as the source materials has been studied. It was established that Al content of the films depends on the growth temperature and at growth temperatures above 470° C corresponds to that calculated for Al₂O₃. The chlorine content of the films increases with the decrease of the growth temperature. The oxygen, aluminium and chlorine mole fractions obtained give a possibility to estimate that about 30 per cent of oxygen remains in OH groups and the mole fraction of AlOCl is about 14 per cent in the case of films grown at 100°C. It has been shown that the mass of aluminium and oxygen deposited during an ALE cycle has a maximum at 300°C while the area covered by oxygen and residual chlorine ions decreases monotonously with the increase of temperature. At the same time the packing density of anions increases and at 470°C reaches the value corresponding to the closest packing of O²⁻.

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TIME DELAYS IN FLOW-TYPE ATOMIC LAYER EPITAXY REACTOR

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Abstract

Time delays of reagent pulses in flow-type ALE reactor have been investigated. It has been shown that these delays limit the growth rate but, on the other hand, they can be used for characterization of the adsorption efficiency of solid surfaces.

Introduction

Kinetic phenomena in atomic layer epitaxy (ALE) have been of great interest because they determine the growth rate and thickness uniformity of the grown films. A number of experimental techniques have been used for investigation of transient effects in ultra-high vacuum reactor [1-7] as well as in flow-type growth equipment [8-13]. Most of the adsorption and desorption processes taking place in these two ALE systems are very similar. However some specific phenomena can be observed in horizontal flow-type reactor. Data published by Hyvärinen et al. [8] show the existence of reagent pulse time delays depending on the exposition sequence. Unfortunately, to the best of our knowledge, no detailed studies of this phenomenon have been published. Therefore in this paper the time delays taking place during ALE growth of Al₂O₃ have been taken under consideration.

Experiment

Experiments were performed in a horizontal low pressure (200-300 Pa) reactor [14] using Ar as a carrier gas and AlCl₃ and H₂O as the source materials. Quartz crystal mass monitor was used for investigation of transient processes. To obtain information about time delays an adsorber consisting of a set of 0.1 mm stainless steel plates covered with Al₂O₃ was placed between gas inlets and mass sensor (Fig.1). The plates were parallel to the reactor axis and one to another. The distance between the plates was chosen equal to 2.5 mm while the width of them was limited by the cross section of the reactor tube. Keeping the distance between gas inlets and mass sensor constant the length of the adsorber was varied to separate the effects of surface reactions and uncontrolled gas-phase reactions.



Fig.1. Schematic diagrams of ALE reactor for investigation of time delays of reagent pulses.

The pulses of AlCl₃ and H₂O were injected into the reactor alternatively using electromagnetic valves. The velocity of the gas flow in the reactor was equal to 4.3 m/s. The purge times between source material pulses were chosen long enough to avoid intermixing of active gases. Doses of H₂O were kept constant while the temperature of the AlCl₃ container was varied to investigate the effect of the source material pressure on the time delays. The film mass deposited onto the quartz mass sensor was plotted with time resolution of 1 s. The time delay caused by the recording system was equal to 1.00±0.05 s. To minimize temperature effects the adsorber and the mass sensor were kept at equal temperatures stabilized with the accuracy of ±0.3°C.

Results

Typical time dependence of the film mass deposited onto the mass sensor at different AlCl₃ pressures is shown in Fig.2. As one can see, significant time delays are evident even if there is no adsorber in the reactor. At the same time the mass of the adsorbate deposited during a cycle saturates at a common value independent of the partial pressure of AlCl₃. During delay time the transmission of adsorber is small in comparison with this value. Thus time delays can be easily obtained from the curves. Fig.3 demonstrates that delays increase with the decrease of AlCl₃ pressure as well as with the increase of adsorber length. At high AlCl₃ pressures the delays are close to

those caused by the recording system. Therefore the effect of the finite flow rate of carrier gas can be neglected.

It was confirmed experimentally that in the case of short (<10s) purge times and high H₂O doses delay times depend on the purge time. This is due to incomplete evacuation of H₂O from the reactor. During the registration of experimental data shown in Fig.2 and 3 this effect was avoided using optimum doses of H₂O and long (>100s) purge times between H₂O pulse and following AlCl₃ pulse. However, dewpoint measurements of carrier gas indicate that H₂O background with partial pressure of 10⁻²-10⁻⁴ Pa exists at the output of the reactor even if there was no preceding H₂O pulse.



Fig.2. Time dependence of film mass deposited onto quartz crystal mass monitor in the case of absence (a) and presence (b) of adsorber in reactor.

Discussion

Fig.3 demonstrates a significant increase of time delays with increase of adsorber length. Rough estimation of the effect of different processes enables us to conclude that no decrease of the flow rate nor gas phase reactions can cause this behaviour. Thus the surface processes may be the main reason for the delays. Indeed, if adsorber is long enough, all the reagent molecules should be trapped by the adsorber until its surface is not saturated by the reagent. Duration of this process is limited by the area of active surface, density of adsorption sites, partial pressure of reagent and flow rate of carrier gas. It has been shown that in case of sublinear adsorption isotherm and at initial wave



Fig.3. Time delay as a function of pressure of AlCl₃ (equilibrium pressure in evaporation cell) at different adsorber lengths l_A . t_0 represents the time delay caused by mass-voltage converter.

front limited by the longitudinal diffusion the propagation rate of adsorption wave can be described using Wilson's law [15]:

$$U = \frac{\nu n}{n + N'},\tag{1}$$

where U is the propagation rate of adsorption wave, v is the flow rate of carrier gas, n is the initial concentration of active particles in carrier gas and N' is the concentration of active particles which have to be adsorbed to attain equilibrium between solid surface and gas phase.

Further we shall deduce a relation between N' and surface density of adsorbed particles N for the adsorber used in this study. We assume that finite diffusion length of AlCl₃ molecules in gaseous phase does not limit their arrival rate onto the adsorber surface. Indeed, using Rozanov's data [16] we found that even at minimum adsorber length the transversal diffusion length of AlCl₃ exceeds more than five times the half distance between the adsorber plates.



Fig.4. Time delay as a function of adsorber length at different pressures of AlCl₃ (equilibrium pressure in evaporation cell).

Let h be the distance between the plates and a and dl be the width and the elemental length of the plates, respectively. Assuming that h << a we get N'hadl – Nadl and N' – N / h. Substituting N' in Eq.1 and taking into account that $t_d - l_A'/U$, where t_d is the delay time caused by adsorber and l_A' is the effective adsorber length, we get:

$$t_d = \frac{l_A}{v} + \frac{Nl_A}{nvh} . \tag{2}$$

In our experiments $l_A^{\prime}/\nu < 0.02s$ was significantly less than the time resolution and thus we can neglect this term. Consequently we have:

$$t_d = \frac{M_A^i}{nvh} . \tag{3}$$

According to Eq.3 $t_d \rightarrow 0$ at $l_A^{\prime} \rightarrow 0$. However, Fig.2 and 3 show that there are significant time delays even if the adsorber is absent. Thus it must be concluded that the walls of reactor and inlet tube act as an additional adsorber. Presenting the data as a function of adsorber length l_A (Fig.4) one becomes convinced that the effective adsorber

length can be expressed as $l'_A = l_A + l_0$, where $l_0 = (8 \pm 1)$ mm is the value of l_A obtained by linear extrapolation of the experimental data to the l_A axis. Using Eq.3 we get a formula for time delay t_d observed experimentally:

$$t_d = N(l_A + l_0) / nvh.$$
 (4)

In Eq.4 the second term describes the effect of reactor and inlet tube giving us a possibility to evaluate the reaction design.

It is remarkable that Eq.4 enables us to calculate n / N and thus to estimate the trapping efficiency of surfaces. Moreover, knowing n one can calculate the value of N. However, in this study we could not estimate the value of n because the ejection efficiency of evaporator was unknown.



Fig.5. Ratio of the density of AlCl₃ in the gas phase to the surface density of adsorbed particles as a function of pressure of AlCl₃ (equilibrium pressure in evaporation cell).

Fig.5 shows n / N as a function of equilibrium pressure P of AlCl₃ in the evaporator cell. As one can see our data fall satisfactorily onto a straight line at reagent pressures exceeding 3 Pa. At lower pressures n / N is a nonlinear function of P. This behaviour is unexpected because mass sensor does not indicate any dependence of the final mass of adsorbate on the reagent pressure. Thus the corresponding value of N must be constant and n / N should be a linear function of P.

However, assuming that chemisorption is limited by surface reactions, dynamic balance between adsorbate and reagent gas may occur at the values of N which are lower

than its final level. It is obvious that chemisorption rate is limited by surface reactions at high reagent pressures rather than at low ones. Therefore the dynamic capacity of adsorber surface at low pressures can increase in spite of the fact that the stationary capacity of surface does not depend on P.

Nonlinear behaviour of n / N can be also explained by gas phase reactions decreasing the reagent supply from evaporator to adsorber. Our estimations show that background pressure of H₂O equal to $4 \cdot 10^{-2}$ Pa is large enough to cause the observed nonlinearity. This value coincides with that obtained from our dewpoint measurements.

Unfortunately our experimental data do not enable us to exclude any of the reasons of nonlinearity described above. Additionally, deviations from Eq.4 can be due to longitudinal and transversal diffusion as well as due to finite adsorption front formation time in adsorber. Nevertheless it is clear that time delays of reagent gas pulses can be successfully used for the investigation of growth processes in flow-type ALE reactors.

Conclusions

The data obtained in this study confirm that the finite propagation rate of adsorption front causes significant time delays in flow-type ALE reactors. These delays set limits to the minimum cycle time as well as to the maximum substrate size. At the same time the delays can be successfully used for investigation of adsorption processes. The relation between partial pressure of reagent gas and equilibrium surface density of adsorbed particles can be calculated using experimental data for delay times. One more valuable feature of the delay times is that they can be used as a measure of the quality of the reactor design.

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AP-MOCVD LAYER GROWTH OF ZnO IN THE H₂-Zn(C₂H₅)₂-CO₂ SYSTEM

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Abstract

c-axis-oriented ZnO films have been successfully grown on the fused qurtz and (100)GaAs substrates at 653K. The variation of the texturing and ordering of ZnO films, their surface morphology and coloring with the growth temperature and with the CO₂/DEZ mole ratio change has been observed. The heterogeneous nature of the growth process of ZnO films in the H₂-Zn(C₂H₅)₂-CO₂ system was established and a selective film growth realized.

Introduction

Zinc oxide is an extrinsic n-type A^2B^6 semiconductor with an energy band gap of 3.4eV. It is an excellent material for transparent electrodes and for various applications, e.g. in surface-acoustic-wave devices, optical waveguides, heterojunction solar cells, because of its large piezoelectricity, large optical refractive index and high optical transparency [1-5].

In addition, the interest in ZnO originates from its potential use in heat reflecting windows to enhance energy utilization in buildings [6], as ZnO in its stochiometric composition is transparent for visible light and reflects infrared thermal radiation.

A number of fabrication techniques for growing good-crystalline-quality ZnO films has been developed. Thin ZnO films can be produced by metalorganic chemical vapor deposition (MOCVD) [7], photo-MOCVD [8],spray pyrolysis [9], reactive evaporation [10] and sputtering [9]. It should be emphasized that the techniques are to be preferred that allow one to obtain highly c-axis oriented and epitaxial ZnO thin films and to realize a selective film growth of ZnO at low substrate temperatures.

In this paper the results about ZnO films deposited on fused quartz and (100)GaAs substrates by MOCVD at atmospheric pressure (AP MOCVD) by using the oxidation of diethylzinc (DEZ) by gas mixture $H_2+20\%CO_2$ are presented. Hydrogen was used as the carrier. The substrate temperature and CO₂/DEZ mole ratio were varied

systematically as the deposition parameters. The influence of different substrate materials on ZnO film growth was established.

Experimental

The MOCVD system used in this work is shown in Fig.1. The quartz reaction chamber was 40cm in length and 4.5cm in diameter, in which 10cm long susceptor resistance heated from the bottom was used. High purity hydrogen gas, bubbled through DEZ, served to transport its vapor to the reactor. It is indispensable to note that DEZ and CO_2 were mixed before their entering the reaction chamber. ZnO films were deposited in the 433-773K temperature range. The film thickness was determined by a gravimetric



Fig.1. Schematic diagram of the growth system used for ZnO AP-MOCVD growth.

Table 1. Substrate cleaning procedures

Substrate	Cleaning procedure	
****===================================		
GaAs	 Wash in boiling isopropyl alcohol; 	
	(2) 2min etch in 1:4:1 H ₂ O ₂ :H ₂ SO ₄ :H ₂ O	
	at 45°C;	
	(3) Water wash and blow dry.	
Fused quartz	(1) 24h etch in K ₂ Cr ₂ O ₇ :H ₂ SO ₄ ;	
	(2) Boiling in K ₂ Cr ₂ O ₇ :H ₂ SO ₄ ;	
	(3) Water wash;	
	(4) Wash in boiling isopropyl alcohol;	
	(5) 15min in thermostat at 120°C.	

technique and checked by the interference measurements. The substrate cleaning procedures used prior to the growth, are detailed in Table 1.

The typical growth conditions of ZnO films were the 40 ml/min hydrogen flow through the DEZ bubbler, the temperature of which was varied, 80 ml/min of $H_2+20\%CO_2$, and a total hydrogen flow 1.0 or 1.6 l/min. As-grown films were examined visually under an optical microscope. Further, a physical characterization was carried out using scanning electron microscopy (SEM) and reflection high-energy electron diffraction (RHEED).

Results and discussion

The most troublesome aspect of AP-MOCVD of ZnO in the DEZ/CO₂/H₂ system is related with the deposition of a white fallout on the tube walls upstream from the growth site at ambient temperature after the mixing of DEZ and CO₂. Probably this phenomenon is caused by a high content of water and oxygen in CO₂ used in this study, as DEZ is chemically very reactive and at temperatures near to ambient it formes complexes with H₂O [12] and reacts with O₂ [13]. The reactions of interest in the present case are:

1. DEZ/H₂O₂/H₂ system At room temperature, in the gas stream $(C_2H_5)_2Zn + 2H_2O = Zn(OH)_2 + 2C_2H_6$ At the surface at high temperatures (400°C) $Zn(OH)_2 = ZnO + H_2O$ $ZnO + H_2 = Zn(v) + H_2O$ 2. DEZ/O₂/H₂ system $(C_2H_5)_2Zn + 7O_2 = ZnO + 4CO_2 + 5H_2O$ $ZnO + H_2 = Zn(v) + H_2O$

The undesirable deposition of the material before the growth chamber led to a nonreproducible growth and to nonuniformities in the properties of the layers produced. The influence of the premature reactions was partially suppressed by optimizing the construction of the gas mixing device and the time during which the gas was in transit from the point of mixing to the susceptor.

The growth rate of ZnO on the fused qurtz substrate as a function of temperature is shown in Fig.2. The CO_2/DEZ mole ratio 49 and the total hydrogen flow of 1.0 l/min were used. The dependence is remarkably strong and the shape of the curve indicates that at low temperature the deposition is kinetically controlled. At high temperature the deposition rate drops due to thermodynamic factors, including the instability of ZnO in the presence of hydrogen.

The growth rate of ZnO films at 653K was dependent on the substrate material employed (Fig.3). On the GaAs substrate the growth rate depended on the growth time,

while at the beginning of deposition the growth rate was lower than on the fused quartz substrate and it increased slowly up to the 40 min growth time or 0.1µm thickness. Further, the growth rate of ZnO on GaAs substrate stabilized, but remained still



Fig.2. Dependence of the growth rate of ZnO (on fused quartz substrate) on temperature.



Fig.3. ZnO film thickness as a function of the growth time on different substrates.

somewhatlower than on the fused quartz. We suggest that the stabilization of the growth rate took place after a continuous layer of ZnO had formed on the GaAs substrate surface. The established growth rate dependence on the substrate material indicates the heterogeneous nature of the growth process of ZnO films in the DEZ/CO₂/H₂ system.

The increase of the growth temperature caused the increase of the growth rate difference (in the region of slow growth) on different substrate materials. It is necessary to emphasize that the conditions for the growth of ZnO films only on quartz, not on (100)GaAs, were established and a selective growth of ZnO films was realized.

The variation of the crystal structure, surface morphology and coloring of ZnO films depending on the growth temperature and the CO₂/DEZ mole ratio has been observed. A ZnO film, 2 μ m in thickness, grown at 653 K and at mole ratio 49, was of a brown color, exhibited a typical cellural surface morphology (Fig.4) and gave the diffraction pattern of a well-ordered texture with the [0001] axis normal to the surface (Fig.5). The presence of forbidden {000(2n+1)} reflections in the pattern indicates the double periodicity in the [0001] direction. The diffraction pattern shows the contraction of the lattice of about 4-6 per cent. At the same time, the broadening and splitting of the reflections indicates that the films consist of thin layers with stacking faults. We suggest that here such a structure of ZnO films forms as the result of Zn excess in the films. It should be noted that there is no evidence of the presence of Zn as a separate phase in the films. Probably there is a layered Zn_{1+x}O solid solution and it is the excess of Zn that causes the stacking faults.



Fig.4. Scanning electron micrograph of a 2 µm-thick textured ZnO film.

The increase of the growth temperature and the $CO_2/DE2$ mole ratio caused the increase in the film surface roughness, the change in the crystal structure and also in the film coloring. The films grown at 683K had a light-brown color, while those grown at 733 K, a white color, both films being polycrystalline. At the same time cellural surface morphology of films disappeared gradually. A slow variation of the crystal structure, surface morphology and coloring of ZnO films, depending on the CO_2/DEZ mole ratio was observed. The increase of the mole ratio from 49 to 82 caused the brightening of the film color and some increase in the film surface roughness, whereas the diffraction pattern characteristic of the texture remained, though some disorder of orientation took place. The ZnO films grown at the mole ratio 100 had a light-brown color too, but on the diffraction pattern the reflections from the texture with the axis {1011} added to the rings from the polycrystal. The diffraction pattern from a very thin (about ten lattice parameters thick) film, grown on the GaAs substrate, showed that the polycrystalline film growth is three-dimensional from the orientation of the crystallites.



Fig.5. RHEED pattern from a textured ZnO film.

It seems inexplicable that the 3D-growth observed for polycrystalline films should be valid at lower temperature for textured films as well. It is more reasonable to assume that there are different growth mechanisms and for textured films with Zn and O sublayers parallel to the substrate surface layer-by-layer growth is valid. The change of the growth mechanism would be explainable when the variation of the interaction between the substrate surface and DEZ, CO₂, as well as the intermediates is considered. But no difference was observed in the structure of the films deposited in the same conditions on different substrates. We conclude that there is more than one sequence of the reaction steps leading to the formation of ZnO from the starting materials. The variation of the growth temperature and the CO₂/DEZ mole ratio leads to various dominating reaction sequences, changes the way of how Zn and O are built in the growth mechanisms.

In this study, the existence of zinc propionate as the intermediate compound and as the result of reaction between DEZ and CO₂ in the gas stream was not established Further investigations are needed to establish the detailed growth mechanism of ZnO films in the H_2 -Zn(C₂H₅)₂-CO₂ system.

Conclusion

To sum up, c-axis-oriented ZnO films have been successfully grown on the fused quartz and (100)GaAs substrates at 653 K. The variation of texturing and ordering of the ZnO films, their surface morphology and coloring with the growth temperature and with the CO₂/DEZ mole ratio change has been observed. The heterogeneous nature of the growth process of ZnO films in the H₂-Zn(C₂H₅)₂-CO₂ system was established and a selective film growth realized.

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V-CENTRES IN PLASTICALLY DEFORMED CaS

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Abstract

Several types of hole V-centres have been observed by the EPR-method in plastically deformed CaS-polycrystals after the X-irradiation at 77 K. The dominating centres V⁻ and V_{SH} are formed when the hole is trapped by a sulphur anion near the isolated cation vacancy or near the cation vacancy associated with an SH-group. The thermal destruction of the V⁻- and V_{SH}-centres occurs at 120-285 K and at 170-210 K respectively. In the case of V⁻-centres it is due to hole jumping between cation vacancies in the areas of high defect density and also due to conventional hole liberation into the valence band in the case of well separated V⁻-centres. The isolated cation vacancies are easily transformed into the associates V_C -(SH)⁻ by heating them up to 450-650K. These associates disappear completely after the samples are heated above 700 K.

Introduction

Calcium sulphide is a well-known base for a variety of luminophors. The properties of CaS-based luminophors are determined not only by different activators and co-activators but also by the intrinsic lattice defects like cation and anion vacancies developed in luminophor synthesis. And yet there are no reliable data on cation vacancies or their associates with impurities in CaS available **thouse** point defects in Alkaline Earth Sulphides have been studied for years. The fact can be accounted for by the want of sufficiently large CaS-single crystals (the existing ones are not widely available) as well as by the inefficiency of the magnetic resonance methods in precise point defect studies of powder samples or by inadequate temperatures in EPR measurements (too high - 77 or 300 K).

The first successful study of cation vacancies and their associates with impurities with EPR at helium temperatures was carried out at the Department of Experimental Physics at Tartu University. A family of paramagnetic defects of similar properties was discovered in CaS-polycrystals activated with haloid ions or alkaline metals after Xraying the samples at 77K. Structural defects which are present in samples become paramagnetic ones when a hole is captured by the sulphide anion next to cation vacancy associated with a haloid ion (Cl^- or F^-) or by the sulphide anion next to Na⁺ or Li⁺

37

substituting Ca^{2+} [1]. The centres observed are of axial structure: $Hal^--V_C-S^-$ or $S^{2-}-M_{Ca}^+-S^-$, where Hal is for Cl or F and M is for Na or Li. We called these defects V_{Cl} , V_F or [Na]⁰, [Li]⁰ on the analogy of the well-known hole V-centres in Alkaline Earth Oxides. However, we must point out here that isolated cation vacancies with captured holes (i.e., V⁻-centres) cannot be detected in CaS-polycrystals with any chemical or thermal treatment. Yet in the course of our experiment we could find an easy way of producing cation vacancies by plastic deformation (pressing) of CaS-polycrystals. Plastic deformation, however, produces besides isolated cation vacancies some associates of defects, the cation vacancies being involved in. After excitation of samples when holes are captured by defects, different paramagnetic centres are formed, V⁻ being the dominating one.

The results of EPR-study of hole V-centres in plastically deformed samples and some properties of cation vacancies are reported in the present paper.

The objects, instrumentation, and experimental methods

Calcium sulphide of high phase purity (up to 99,4%) and of luminophor purity grade was prepared by the reduction of CaSO₄ with flowing purified hydrogen according to the method described in [2]. The initial CaSO₄ was precipitated from high purity grade Ca(NO₃)₂ and (NH₄)₂SO₄ solutions, especially purified before the reaction by organic extracting agents to remove transition and heavy metals. Alkaline metals were removed by repeated washing of precipitated CaSO₄ with distilled water.

Some quantities of CaS were doped with haloid ions or alkaline metals. The required amounts of dopants were added and the samples were heated with 2-20% of sulphur under flowing argon at 900-1150°C for 30-45 minutes. Then the samples were cooled out of furnace under flowing argon.

The plastic deformation of samples was effected by a hydraulic press at room temperature. The pressure applied varied from 100 to 2000 MPa. The pellets produced by pressing were crushed and ground into powders before carrying out the EPR-measurements.

The EPR-spectra were obtained with a home-made X-band (8,875 GHz) spectrometer of 100 KHz magnetic field modulation. An "Oxford Instruments" ESR-9 continuous flow helium cryostat was used to keep the samples at necessary temperatures. Pulse annealing of the samples was performed to determine the thermal stabilities of the V⁻-centres and of the cation vacancies. With the temperatures below 300 K, the pulse annealing was carried out in the cryostat directly, and by higher temperatures (300-800 K), a special separately mounted electric furnace was employed. In pulse annealing, samples were fast heated to the required temperature kept at the level for certain time (2 minutes), and fast cooled down to the temperature chosen for measurement (35 K for V-centres). To make defects paramagnetic, the samples were X-irradiated before the annealing (50 kV, 18 mA, W-anode) at 77 K. To investigate ionic processes at the temperatures above 300 K at which the holes escape from V⁻centres,

the samples were X-rayed at 77 K after each step of annealing to populate the cation vacancies with holes. The X-irradiation of samples was continued until the EPR-signal intensity stopped to increase (usually 1h).

The experimental results and discussion

The EPR of CaS before deformation demonstrated that there was a minute quantity of Mn^{2+} and Cr^{3+} -ions within a cubic symmetry surrounding. After X-irradiation at 77 K weak signals of $[Na]^{0-}$ and $[Li]^{0-}$ centres could also be observed which indicate a mild contamination of CaS with the alkaline metals. V_{F^-} and V_{Cl^-} centres were observed in the samples doped with these haloids.



Fig.1. Variation in the V-centre concentration with the amount of pressure applied (a) and with the time of X-irradiation at 77 K (b).

After mechanical deformation (grounding, smashing, pressing) the F⁺-centres become detectable (F⁺ stands for the electron trapped at anion vacancy). The F_C⁻centres could also be detected, but after the deformed samples had been X-rayed (F_C⁻ stands for the electron trapped at the associate of anion and cation vacancies). The sharp single isotropic lines with g=2.0033 (for F⁺) and g=2.0019 (for F_C⁻) corresponding to these centres could be observed in EPR-spectra at a low level of microwave power provided that the temperature is not too low.

Besides the F^+ and F_C^- -centres several anisotropic centres of similar properties are formed in plastically deformed CaS. These centres observable after Xirradiation of the samples at 77 K increase in concentration steadily when the pressure to polycrystals is increased (See Fig.1). After the excited samples had been annealed to different temperatures their EPR-spectra analysis revealed three centres of axial symmetry of g-tensor formed under plastic deformation. The weak lines of these centres corresponding to parallel components of g-tensor are strongly overlapping with the F⁺centre signal and with signals of some unknown defects within the range of g=2.0. The more intensive lines connected with the perpendicular g-tensor components partly overlap with each other (See Fig.2). The *g*-tensor components and other parameters for these defects designated V_0 , V_1 , V_2 are given in Table 1. The *g*-values of V_2 , V_1 , and V_0 are very close to those of V_{Cl} - and V_F -centres. All the centres are observable at high levels of microwave power and at the same optimal temperatures of 25-35 K (except in case of $[Na]^0$ - and of $[Li]^0$ -centres). Hence, the V_2 , V_1 , V_0 and V_{Cl} , V_F centres are of similar structure involving cation vacancy.

To prove it is the V_2 -centre that is the isolated cation vacancy with a hole trapped on it, i.e., a V⁻-centre, the following experimental evidences can be given:

1. The V₂-centre is characterized by the highest temperature of hole liberation of the group studied (See Fig.4). It fully disappears at 285 K, while the V_{Cl}- and V_F-centres are destroyed at a temperature as low as 215 K. Therefore, there is no charge compensating defect in the close vicinity of the cation vacancy in comparison with the V_{Cl}- and V_F-centres.

2. The g_{\perp} -value of the V₂-centre is the smallest one in the whole family of Vcentres. The following expression for g is known to be true for the analogous axial centres [3]:

$$g_1 = 2.0023 \cdot (1 - 2\lambda / \Delta),$$

where λ is the spin-orbit interaction constant (for S⁻-ion $\lambda < 0$), and Δ is the energetic interval between the ground state P_Z and the excited states P_X and P_Y which are splitted by the axial crystalline field. The maximum Δ -value can be expected in case of the V⁻- centre, and hence, the minimum value of g_{\perp} .



Fig.2. The EPR-spectrum (T_{OBS}=35K) of the V-centres in plastically deformed CaS polycrystals: full scale (a) and the region of g_{\perp} (b). The averaged spectrum (T_{OBS}=145K) of V⁻-centre (c).(ν =8876,2 MHz).



Fig.3. The intensity variation of axial and averaged spectra of V^- -centres depending on the temperature of observation (the curves are given on different arbitrary scales). An analogical curve for V_{SH}-centre is shown for comparison (dashed line).

3. The motional averaging of the EPR-spectrum of the V₂-centre can be observed. With the temperature rise up to 100K, the axial spectrum lines broaden and disappear, and thereafter the wide isotropic line (Hpp=35G at T_{OPT}=145K) with $g = (2g_{\perp} + g_{\parallel})/3 = 2.084$ becomes detectable in the temperature range 110-170 K (See Fig.2 and Fig.3). The spectrum transformation described above indicates hole jumping between sulphur anions surrounding the cation vacancy at the temperatures above 110 K. Hence, there are not any defects in the close vicinity of the V_C. It is to be noted that no motional averaging could be observed in case of V₀, V₁, V_C, V_F-centres. The EPR-spectra of these centres, on the contrary, disappear almost at the temperature of thermal destruction (hole liberation).

centre	T ^{obs.} , K	g⊥	8	Tescape , K
[Na] ⁰	8 - 11	2,2354±0,0005	2,003	120 - 160
[Li] ⁰	14 - 18	2,1702±0,0005	2,002	120 - 160
VF	20 - 35	2,1314±0,0005	2,002	160 - 210
VCI	20 - 35	2,1317±0,0005	2,002	180 - 215
$v_{SH}^*(v_0)$	20 - 35	2,1342±0,0020	2,002	120 - 160
$V_{SH}(V_1)$	20 - 35	2,1327±0,0020	2,002	160 - 210
V-(V2)	20 - 35	2,1240±0,0020	2,002	up to 285

Table 1. The V-centres parameters in CaS.



Fig.4. The electron-hole processes at pulse annealing of plastically deformed CaS (at 1250 MPa pressure). Variation of V-centre quantities with the temperature of pulse annealing.



Fig.5. Ionic processes in plastically deformed CaS (pressure applied at 1250 MPa). Annealing time at each step – 2min. F⁺– and F_C^- -centres measured after X-irradiation at 300K, and V⁻– and V_{SH}-centres – after X-irradiation at 77K. The time of X-irradiation was sufficient for maximal paramagnetic defect formation.

The V₁-centres possess axial symmetry, and the g-tensor value of these centres is close to that of V_{Cl} and V_F-centres. Moreover, the thermal stabilities of V₁, V_{Cl}, V_Fcentres are practically alike (See the Table 1). Summarizing the facts mentioned above, we consider the structure of the V₁-centre to involve some defect with an effective charge +1 at the anion position nearest to the V_C. We suppose this defect to be the molecular ion (SH)⁻ as hydrogen may become incorporated in the CaS-lattice in the course of the material synthesis (Part 2).

Another fact in favor of the (SH)⁻being present near the cation vacancy in the V₁-centre is the transformation of all the isolated cation vacancies (V₂, or V⁻) into the associates (V₁- centres) after the deformed samples have been annealed at 500-675 K (See the text below). The defect transformation can be explained by some impurity migration through the lattice, which gives rise to the V₁-associate being formed. The low temperature at which the migration takes place indicates that this impurity must be a small ion of light weight, most likely a proton. We have tried to detect the superhyperfine structure (SHFS) caused by the proton in the EPR-spectrum of the V₁-centres prevailing in number. But we failed to detect any SHFS, probably due to the EPR-line being too broad in comparison with the splitting value. That happens when the V_F-centres in the plastically deformed samples are studied and the SHFS from ¹⁹F becomes unobservable because of the broadening of the EPR-lines due to multiple defects generated under deformation.

An alternative model of the V_1 -centres involves the associate of the cation vacancy with (OH)⁻-ion substituting the nearest to V_C sulphide-anion (S⁻-V_C-(OH)⁻). To check this model samples with different oxygen contents were prepared and studied. Oxygen was introduced by annealing the samples at a high temperature (900-1100°C) either with limited oxygen access or with the admixture of (NH₄)₂SO₄ and other oxygen sources. The samples obtained were chemically analyzed for their S²⁻ content, which varied from 74% to 99.4%. After the samples being pressed and X-irradiated at 77K the relative quantities of V₁ and V⁻-centres were evaluated. The relative quantity of V₁centres does not seem to depend on the level of the oxygen concentration, as the V₁/V⁻ ratio is constant regardless of the S²⁻ and O²⁻ contents (the quantity of V⁻ decreases along with that of V₁ with the S²⁻contents decreasing). Thus, oxygen does not take part in the V₁-centre formation.

Therefore, we suppose the V₁-centres to possess the following structure: S⁻-V_C-(SH)⁻, where the (SH)⁻-molecular ion plays the role similar to that of (OH)⁻ in the Alkaline Earth Oxides. So we shall use the symbol V_{SH} for V₂. Although we have not succeeded in detecting hydrogen in H⁰-form in the initial CaS yet it should be present probably or admixed in some non-paramagnetic form.

Another V-centre observed in plastically deformed CaS was designated by V_0 . The thermal stability of V_0 (for a hole liberation) is less than that of V_{SH} -centres (See Fig.4). After annealing the deformed samples at temperatures from 500K to 675K the quantity of V_0 -centres increases as well as that of V_{SH} -centres. The facts represented above allow us to suppose that the V_0 -centre is an associate of the V_{SH} with some additional charge compensating defect.

There are some common features in the V-centres described. We could observe the V-centres in paramagnetic states, with a hole being trapped on the appropriate lattice defect containing the cation vacancy. We should emphasize here that the structural defects were produced by plastic deformation, with the X-irradiation at 77K used only to transform the defects into the paramagnetic form. No structural defects can be created by CaS X-irradiation, that explains why we have never seen the V₂, V₁, V₀-centres in X-irradiated but undeformed samples. Moreover, the V-centre concentrations were observed to increase steadily with pressure increase to polycrystals (See Fig.1). The single-stage character of V-centre accumulation under the X-irradiation of the deformed samples (Fig.1) should also be noted here.

The thermal electronic and thermal ionic processes at V-centres fortunately proceed within different temperature ranges in CaS. Fig.4 illustrates the results of the V-centre pulse annealing (electron-hole processes). The quantity of V⁻-centres decreases steadily with the temperature rising from 120 K to 285 K. V₀ and V_{SH}-centres are destroyed with the temperature reaching 160 K and 210 K respectively. The thermal destruction of V⁻-centres within the temperature range of 120-285 K is accompanied by the number of F_C⁻-centres decreasing, though the F_C⁻-centres are stable even at room temperature range of the V⁻, V_{SH} and V₀ thermal destruction (Fig.4). The data presented will be easily understood when the V⁻, V_{SH} and V₀-centre thermal destruction is associated with hole escape from the centres. It should be pointed out that there is a very low probability of electron-hole recombination at the V⁻-centres due to their effective negative charge.

The unusually wide temperature range of the V⁻-centre thermal destruction might be accounted for by the presence of some interfering defects in the vicinity of V-centres in plastically deformed samples. These defects could affect the potential barrier of trapped hole transition to valence band, the barrier being decreased or increased depending on the charge and location of the interfering defect. The assumption of the interfering defects is in agreement with a very large width of EPR-lines observed for g1 -components of V⁻centres (Δ Hpp= 5 G at, T=35 K) exceeding that of V_F and V_{C1} in undeformed samples almost by an order of magnitude. The formation of vacancy pairs $V_C \cdot V_A$ detected by EPR as F_C -centres is an indirect supporting factor for the possibility of the anion vacancies being located not far from cation vacancies. Nevertheless, it is important to note the character of thermal destruction of VF, VCI and [Na]⁰, [Li]⁰-centres being almost unchanged after CaS-sample deformation: most centres disappear at the same temperature both in the deformed and undeformed samples. Thus, we can suggest another explanation for the thermal destruction of V-centres occurring in the wide temperature range. The temperature range may be so wide due to hole jumping between cation vacancies situated not far from each other. As we observed the motional averaging of the EPR-signal above 110K, the hole rotating around

the cation vacancy is very likely to be retrapped by another cation vacancy located in the vicinity of the one the hole belonged to. The probability of hole transfer to more distant cation vacancy increases with the temperature increase. As a result a hole may be transported to some recombination centre where it annihilates with trapped electron. Hole jumping between cation vacancies is likely to take place in the regions of high density of defects. This mechanism should be responsible for the V⁻-centre destruction within the temperature range 120–215 K (the temperature of V_{Cl} and V_F destruction is suggested as the upper limit). The conventional mechanism of hole release into the valence band is probably realized at the temperatures as high as 240–285 K.

We determined the thermal stability of the isolated cation vacancies and the associates of the cation vacancies with SH⁻-groups or anion vacancies in plastically deformed CaS. For this purpose the relative numbers of the V⁻, VeH and Fc⁻, F⁺centres were measured in the course of pulse annealing of the samples. The results are shown at Fig.5. The isolated cation vacancies disappear at temperatures between 500 K and 750 K. This process is accompanied by the formation of the associates V_C-(SH)⁻. The sum of numbers of V_C and V_C-(SH)⁻ is approximately constant between 500K and 675 K. Therefore, the transformation of V_C to V_C-(SH)⁻ associates is likely to occur. The transformation can proceed both as a result of the cation vacancies migration and their capture by the (SH)-impurity and as a result of the capture of the migrating hydrogen (protons) by cation vacancies. When the moving entities were cation vacancies, formation of the new vacancy pairs VC·VA could be observed as the anion vacancies exist up to 650 K. But we could prove that that was not the case - the number of the vacancy pairs VCVA remained constant at those temperatures (See Fig.5). Hence, the transformation of VC to VSH is due to the capture of migrating impurity (protons) by V_C. It is worth mentioning that the disappearance of the anion vacancies observed in the interval 550-675 K may also be caused by the same reason.

The associates $V_C V_A$, $V_C - (SH)^-$ and the remaining isolated cation vacancies are annealed over a narrow temperature range 675-750 K. These defects differ by their structures and effective charges. So, one may suppose that all the centres containing cation vacancies are destroyed due to the annihilation of migrating calcium interstitials with the cation vacancies.

Conclusions

The method of plastic deformation of samples enabled us to create several lattice defects in CaS which had not been available for investigation due to other methods failing to produce these defects in sufficient concentrations. However the method used has also shortcomings. We obtained galaxies of mutually affecting defects. As a result we had broadened EPR-lines and abnormally wide temperature ranges of the electron-hole thermal processes. All the features mentioned above sometimes make the result interpretation difficult and force us to seek for other less radical means of defect production.

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ALE MODEL CONSIDERING THE SURFACF STRUCTURE OF THE GROWING BINARY COMPOUND

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Abstract

MBE growth of A^2B^6 compounds in the case of ALE is modelled mathematically. Linear dependence of the desorption energy of the nonmetallic component of the compound on the surface coverage is considered. It is shown that the surface reconstruction caused by growth temperature variation results in abrupt change of the growth rate.

One of the main parameters describing the growth process of binary compounds (A²B⁶, A³B⁵) is the desorption frequency λ - the number of atoms desorbed from one filled adsorption site per time unit. The desorption frequency is determined by the temperature and the binding energy of the atoms on the surface. In the studies known to us the desorption energy determined from MBE and ALE experiments has been regarded to be independent of the surface coverage Θ [1-4]. Nevertheless, a different conclusion follows from the investigations of the structure and coverages of the polar surfaces of $A^{3}B^{5}$ compounds. It is known that the change of Θ_B of an ordered (100) surface with temperature does not exceed 0.5 monolayers, whereas the coverage with B atoms of about a guarter of a mnonolayer remains on the surface until the evaporation of the compound [5]. It has been found that the desorption energy of B atoms on the surfaces of A³B⁵ compounds increases linearly with decreasing coverage Θ_B [6]. We suppose that it is valid also for A²B⁶ compounds. The linear dependence of the binding energy of B atoms on the coverage means that when B beam impinges on the surface, the desorption frequency of B atoms increases exponentially with the increase of Θ_B . In the case of simultaneous deposition of the components of the compound (conventional MBE) there persists a constant surface coverage corresponding to the molecular beams used, therefore the desorption frequency of B atoms remains constant during the growth process. In the case of cyclic growth when the components of the compound are deposited alternately (ALE), the surface coverage varies periodically and the changes of the desorption frequency are significant in describing the growth

process.

The relation of the desorption energy of B atoms and the coverage enables to determine the dependence of the growth process on the equilibrium surface structure of the growing compound. It has been established that according to temperature variation the polar surfaces of the compound form a number of stable ordered structures, each corresponding to a certain temperature region and characterized by a certain surface coverage. The dependence of the structure and coverage of (100) surface of A^3B^5 compounds on temperature has been determined [5]. On the basis of above–given it is evident that the transitions from one stable surface structure to another, which occur in relatively narrow temperature intervals, may lead to jumps in the desorption frequency of B atoms and hence, to abrupt changes in the growth kinetics. In the following it will be shown that supposition of the influence of the surface structure on the growth process lies in agreement with the temperature dependence of the growth rate known from experiments and so, the knowledge about the surface structures of the growth kinetics.

In the present paper the film growth is described by the equations

$$\frac{d\kappa_A / dt - v_A \Theta_B - \lambda_A \Theta_B}{d\kappa_B / dt - v_B \Theta_A - \lambda_B \Theta_B}$$
(1)

where κ_A and κ_B are the numbers of the atomic layers of A and B components, respectively, and Θ_A and Θ_B are the surface coverages by the atoms of respective type, while

$$\begin{array}{l} \Theta_A + \Theta_B = 1 \\ \Theta_A = \kappa_A - \kappa_B \end{array} \right\}.$$

$$(2)$$

It is assumed that the desorption frequencies λ and the adsorption frequencies ν depend exponentially on the reciprocal temperature. The linear dependence of the desorption energy of B atoms on the surface coverage gives for the desorption frequency of B atoms

$$\lambda B = \lambda B0 \exp(-\Theta_A \Delta E / kT) \tag{3}$$

where ΔE is the difference between the desorption energies corresponding to the coverages $\Theta_A = 1$ and $\Theta_A = 0$, k is the Boltzmann constant and T is the substrate temperature.

In the following the equilibrium coverage of the surface not exposed to molecular beams is called zero-coverage Θ_A^* . The zero-coverage is determined from the condition

$$\left[dK_{A} / dt \right]_{\Theta_{A}^{\star}} = \left[dK_{B} / dt \right]_{\Theta_{A}^{\star}} ; V_{A} = V_{B} = 0.$$
 (4)

The desorption frequency λ_{B0} corresponding to the coverage $\Theta_A=0$ can be determined using the zero-coverage in the form

$$\lambda_{BO} = \lambda_{A} \left[\Theta_{A}^{*} / (1 - \Theta_{A}^{*}) \right] \exp(\Theta_{A}^{*} \Delta E / kT).$$
 (5)



a

Fig.1. The equilibrium surface coverages with A atoms in A beam Θ_A^A and in B beam Θ_A^B (Fig.1a) and their difference (Fig.1b) as functions of the equilibrium surface coverage without molecular beams (the zero-coverage) Θ_A^{\pm} . T=650K. In A beam $v_{\bf A}$ =50 τ^{-1} , in B beam $v_{\bf B}$ =50 τ^{-1} .

Fig.1a: $1 - \Theta_A^A$. The curves corresponding to $\Delta E = 1eV$ and $\Delta E = 0$ coincide; $2 - \Theta_A^B$, $\Delta E = 1eV$; $3 - \Theta_A^B$, $\Delta E = 0$. Fig.1b: $1 - \Delta E = 0$; $2 - \Delta E = 1eV$. Now the set of equations (1) obtains the form

$$d\kappa_A / dt = v_A (1 - \kappa_A + \kappa_B) - \lambda_A (\kappa_A - \kappa_B)$$

$$d\kappa_B / dt = v_B (\kappa_A - \kappa_B) - \lambda_B 0 (1 - \kappa_A + \kappa_B) \exp[-(\kappa_A - \kappa_B) \Delta E / kT]]$$
(6)

The solutions of this set cannot be expressed by elementary functions. For computer-solving the quantities of the atomic layers κ_A and κ_B are expanded as Taylor series and thereafter Runge-Kutta method is used.

The modelling of ALE growth is carried out as described in [7], where a constant value is assigned to the adsorption frequency of one element during the pulse of this element, while the adsorption frequency of the other element is equalized to zero that time. The desorption frequency of A atoms is taken to be unity, i.e. $\lambda_{A=1}$, and the desorption frequency of B atoms and the adsorption frequencies are measured as ratios to it.

The upper limit for the probable values of ΔE can be considered as half of the dissociation energy of B₂ molecule, which corresponds to the conception of strictly molecular desorption of B₂ in the case of the coverage $\Theta_A = 0$ and strictly atomic desorption in the case of the coverage $\Theta_A = 1$. It is known that at (100) surfaces of binary compounds B atoms are combined into dimers. Therefore the probable energy gain in the case of molecular desorption is evidently to some extent smaller than the dissociation energy. When the values of the dissociation energies [8] are taken into account, the value $\Delta E = 1eV$ used in our calculations is of suitable order of magnitude for A^2B^6 compounds.

At first, the dependence of the film growth on the zero-coverage is regarded in the cases $\Delta E = 0$ and $\Delta E = 1$ eV. The equilibrium coverage under molecular beams is a suitable measure for the growth rate – the film growth per one ALE cycle would be equal to the difference of the equilibrium coverages Θ_A^A and Θ_A^B under A and B beams, respectively, when the desorption of one element does not occur. In the case of high adsorption frequencies the difference between the difference of the equilibrium coverages $\Theta_A^A - \Theta_A^B$ and the growth rate, is small.

The relation of the equilibrium coverage with the adsorption and desorption frequencies is expressed by the equations

$$v_{A} + \lambda_{B0} \exp(-\Theta_{A}^{B} \Delta E / kT) = [v_{A} + \lambda_{A} + \lambda_{B0} \exp(-\Theta_{A}^{B} \Delta E / kT)]\Theta_{A}^{B}, v_{B} = 0.$$

$$\lambda_{B0} \exp(-\Theta_{A}^{B} \Delta E / kT) = [v_{B} + \lambda_{A} + \lambda_{B0} \exp(-\Theta_{A}^{B} \Delta E / kT)]\Theta_{A}^{B}, v_{A} = 0.$$
(8)

Fig.1a presents the equilibrium surface coverages Θ_A^A and Θ_A^B , corresponding to the adsorption frequencies $v_A = 50 \tau^{-1}$, $v_B = 0$ and $v_A = 0$, $v_B = 50 \tau^{-1}$, as functions of the zero-coverage. Fig.1b shows the difference of the respective equilibrium surface coverages. We can see that the changes in the equilibrium coverages (and consequently, also in the growth rate of the film) are small in the real zero-coverage interval $0.25 < \Theta_A^* < 0.75$ in the case $\Delta E = 0$. In the case of coverage dependent desorption energy of B atoms ($\Delta E = 1eV$) the desorption



Fig.2. The temperature dependence of the maximum growth per cycle κ_m . The zero-coverage jumps are : 1 - from $\Theta_A^* = 1/4$ to $\Theta_A^* = 1/2$; 2 - from $\Theta_A^* = 1/3$ to $\Theta_A^* = 2/3$; 3 - from $\Theta_A^* = 1/2$ to $\Theta_A^* = 3/4$. $v_A = 50 \tau^{-1}$ during A pulse and $v_B = 50 \tau^{-1}$ during B pulse.

Fig.2a. The desorption frequency of B atoms remains constant during ALE process and is determined by the temperature and by the zero-coverage only.

Fig.2b. The desorption frequency of B atoms depends on the surface coverage during ALE process.



frequency $\lambda_{\rm B}$ increases rapidly with the decrease of the coverage Θ_A under B beam, the equilibrium between adsorption and desorption is achieved at a smaller deviation of the surface coverage from the zero-coverage, and the dependence of the equilibrium coverage Θ_A^B on the zero-coverage is nearly linear. Since the dependence of the equilibrium coverage under A beam Θ_A^A on the zero-coverage is slight, the dependence of the difference of the equilibrium coverages $\Theta_A^A - \Theta_A^B$ (and thus of the growth rate) on the zero-coverage is nearly linear in the interval 0.25 $\Theta_A^{\rm A} = 0.75$.

In the following the results of ALE growth modelling are presented when the reconstruction of the growing surface caused by temperature variation, is taken into account. We started from the experimental data concerning an abrupt change of the growth rate in the temperature interval (580-610)K from 1.1 to 0.4 monolayers per cycle in the case of ZnSe(100) [9] and in the temperature interval (560-590)K from 1 to 0.5 monolayers per cycle in the case of CdTe(100) [10]. To obtain comparable results the temperature interval of the surface reconstruction is chosen to be (580-600)K in our calculations. The considerations presented in [5] predict the probable zero-coverage jumps $\Theta_A^* = 1/4 \rightarrow \Theta_A^* = 1/2$, $\Theta_A^* = 1/3 \rightarrow \Theta_A^* = 2/3$, $\Theta_A^* = 1/2 \rightarrow \Theta_A^* = 3/4$. The pulse durations are chosen to correspond to the maximum growth per cycle and the pause durations are taken equalled to zero.

The results corresponding to the adsorption frequencies $v_A = 50 \tau^{-1}$, $v_B = 50 \tau^{-1}$ are presented in Fig.2a ($\Delta E = 0$) and Fig.2b ($\Delta E = 1eV$). We can see that the surface reconstruction caused by temperature variation cannot give rise to noticeable reduction of the growth rate, when the binding energy of B atoms does not depend on the coverage. However, if the binding energy of B atoms is coverage dependent, the assumption about the zero-coverage jump accompanying to the surface reconstruction, is in accordance with experiments, when the zero-coverage is less than 1/2 at the lower temperature. It must be noted that the experimentally established high growth rate values (1 monolayer per cycle and more) point out that the ALE growth condition is not valid at lower temperatures, i.e. the A-A and B-B bonds can be formed, which is precluded in our calculations.

The maximum growth rates and their changes in result of surface reconstruction are presented in Table 1 for some adsorption frequencies, whereas the zero-coverage jump and the temperature correspond to these presented in Fig.2b. We can see that the growth rate increases with the increase of the beam fluxes for the both zero-coverages. However, the growth rate jump is almost independent of the beam flux and equals approximately to the zero-coverage change corresponding to the reconstruction, being somewhat less than the zerocoverage jump when the average value of the zero-coverage is less than 1/2, and somewhat exceeding the zero-coverage jump when the average zero-coverage value exceeds 1/2. Table 1. Maximum growth per cycle for the surface coverages corresponding to the stable surface structures, and their change with the surface reconstruction at 600K. $v_A = v_B = v$, $\Delta E = 1$ eV.

Zero coverages Θ_A^* corresponding	Adsorption frequency	Maximum growth per cycle, monolayers		Growth rate jumps caused
to the surface reconstruction		in the case of the lower zero-coverage	in the case of the higher zero-coverage	by the surface reconstruction
$1/4 \rightarrow 1/2$	10	0.695	0.454	0.241
	20	0.794	0.550	0.244
	. 50	0.874	0.634	0.240
	100	0.923	0.681	0.242
1/3 → 2/3	10	0.618	0.280	0.338
	20	0.716	0.372	0.344
	50	0.799	0.458	0.343
	100	0.843	0.503	0.340
	10	0.454	0.183	0.271
1/2 → 3/4	20	0.550	0.277	0.279
	50	0.634	0.360	0.274
	100	0.681	0.408	0.273

Conclusions

1. The abrupt changes of the growth per cycle are in accordance with experiments, if the coverage dependence of the desorption energy of nonmetallic atoms is taken into account.

2. The growth of the film per ALE cycle depends on the equilibrium surface coverage without molecular beams, therefore the growth kinetics is remarkably influenced by the probable surface reconstructions of the growing compound caused by temperature variation. The prognosis of the growth kinetics changes can be carried out using the results of independent experiments determining the surface structures and the corresponding zero-coverages of the necessary compound by LEED and AES or ESCA methods.

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KINETICS OF CYCLIC DEPOSITION OF A BINARY COMPOUND

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Abstract

The dependence of the cyclic growth of A^2B^6 compounds from molecular beams on the choice of the parameters of ALE cycle is investigated on the basis of a mathematical model. It is shown that the coverage dependence of the desorption energy of the nonmetallic component turns the growth process asymmetric in relation to the equilibrium surface coverage. The pulse time of the nonmetallic component and the pause duration after this pulse have remarkable effect on the growth rate.

In our previous study [1] the binary compound growth model of MBE ALE process on polar surfaces was presented. The distinctive feature of this model was the linear dependence of the desorption energy of nonmetallic atoms on the surface coverage. It was shown that the dependence of the film growth on the equilibrium surface coverage without molecular beams (zero-coverage), determined on the basis of our model, was in agreement with that determined from experiments. In the present paper this model is used to deal with the film growth kinetics and possibilities of the deliberate changes of it.

According to the model, the growth parameters are the substrate temperature T, the zero-coverage Θ_A^* corresponding to this temperature, desorption frequencies λ_A and λ_B , adsorption frequencies v_A and v_B of the constituent elements of the growing compound, deposition times t_A^+ and t_B^+ of the components and pause times t_A^- and t_B^- after A and B pulses, respectively. In the following we try to describe the influence of adsorption and desorption frequencies, pulse durations and pause times as quantities adjustable in experiments, on the growth of A^2B^6 compounds. In the present paper the film growth is analysed at a certain constant temperature. It must be mentioned that temperature variation may give rise to abrupt changes of the growth rate caused by the zero-coverage jumps. The time unit used equals to the average life-time of the metal atom on the surface

$$\tau_A = 1/\lambda_A \tag{1}$$

and therefore depends on temperature. Thus, analogically with the paper [1] the adsorption frequencies and the desorption frequency of element B are determined as ratios to the desorption frequency of A atoms.



Fig.1.Dependence of the surface coverage Θ_A (a) and the changes of the numbers of the atomic layers of A and B atoms $\Delta \kappa_A$ and $\Delta \kappa_B$, respectively (b), on the deposition time. B pulse is followed by A pulse. The adsorption frequency of A atoms during A pulse v_A equais to the adsorption frequency of B atoms during B pulse v_B . T=650K, ΔE =1eV, $\Theta_A^* = 0.5$, $v_A = v_B = 10\tau^{-1}$.

Let us consider the film growth during a cycle if the surface is alternately exposed to A and B beams and there is no pause between the pulses of different elements. Fig.1 shows the surface coverage Θ_A variation and the changes of the number of the atomic layers $\Delta \kappa A$, $\Delta \kappa B$ in this cycle, when B pulse is followed by A pulse. The exposition times are chosen so that the surface coverage under molecular beam reaches its equilibrium value. One can see that the coverage dependence of the desorption energy of B atoms turns the growth process asymmetric in respect to the zero-coverage: the difference of the equilibrium coverage under molecular beam from the zero-coverage in the case of deposition of A atoms is considerably greater than in the case of deposition of B atoms. The second essential feature can be observed in changes of the numbers of atomic layers. Since the equilibrium coverage under molecular beam is achieved, the film thickness decreases at a constant rate. During A pulse the decrease rate of the layer is determined by the desorption frequency of B atoms, which decreases with increasing equilibrium coverage under A beam. The decrease of the layer when the surface is exposed to B beam, is determined by the desorption frequency of A atoms, which is independent of the surface coverage. Therefore in the case of long exposition times the decrease rate under B beam exceeds considerably the decrease rate under A beam.



Fig.2. The growth per cycle $\Delta \kappa$ as a function of the pulse time of one element; the pulse time of the other element corresponds to the maximum growth per cycle. T=650K, $\Delta E = 1eV$, $\Theta_A^* = 0.5$, $v_A = v_B = 10\tau^{-1}$.

1 - tA⁺ changes and tB⁺=t⁺B,max;

2 - tB+ changes and tA+=t+A,max.

The growth of the layer proceeds as long as the increment of the number of the atoms of the element deposited exceeds the decrease of the number of the atoms of the other element, i.e. there exist deposition times $t^+A_{,max}$ and $t^+B_{,max}$ during which maximum growth per cycle occurs. These pulse times are determined from the conditions

From the existence of the maximum growth per cycle as a function of pulse times, the question essential for ALE arises: how much is the growth effected by the probable deviations of the deposition times from the times corresponding to the maximum growth per cycle. Fig.2 shows the change of the growth per cycle when the deposition time of one component varies and the other deposition time retains the value corresponding to the maximum growth per cycle. One can see that the dependence of the



Fig.3. The deposition times of A (curve 1) and B (curve 2) atoms corresponding to the maximum growth per cycle, versus the zero-coverage Θ_A^* . T=650K. $\Delta J = 1 \text{ eV}$, $v_A = v_B = 10 \text{ t}^{-1}$.

film growth on the deposition time reflects the asymmetry of the growth process. Under A beam the surface coverage increases rapidly. With the increase of the deposition time such surface coverage values are reached, at which the surface density of suitable adsorption sites is considerably decreased and therefore the following growth up to the equilibrium coverage under molecular beam proceeds slowly. The decrease rate of the layer since the equilibrium coverage is reached, is small, as mentioned above. Really, the growth per cycle does not change since A pulse time exceeds the value of about 0.4 to 0.61° Δ max. In the case of the deposition of B atoms at small deposition time values the growth takes place in the interval where the surface coverage exceeds the zerocoverage. For these coverages the desorption rate of B atoms is small and the growth per cycle increases linearly with the pulse time. In the case of greater deposition times, when the surface coverage obtains values smaller than the zero-coverage, there remains a sufficient number of B adsorption sites and the equilibrium coverage is achieved telatively quickly because of the rapid increase of the desorption rate of B atoms. The following increase of B pulse time leads to considerable decrease of the layer thickness. Thus we can see that the choice of B pulse time has essentially greater effect on the growth per cycle than the choice of A pulse time.

Let us consider how the growth is influenced by the zero-coverage variation. The quantity $(1-\Theta_4^*)$ can be considered as the measure of the growth per cycle. The dependence of the deposition times, corresponding to the maximum growth per cycle, on the zero-coverage is depicted in Fig.3. Comparison of the curves in Fig.3 with the results of [1] shows that despite the growth per cycle decreases with the zero-coverage increase, the decrease of the deposition times may cause the increase of the growth per time unit.

Besides variation of the deposition times, in experiment there is feasible to vary also the beam fluxes impinging on the substrate, and therefore to change to some extent the adsorption frequencies: the adsorption frequency increases with the beam flux until the time to form the bond on the surface exceeds the time interval between the incidence of two successive atoms on one adsorption site. The dependence of the maximum growth per cycle on the adsorption frequency of one element, when the adsorption



Fig.4. The maximum growth per cycle $\Delta \kappa_{max}$ as a function of the adsorption frequency v of element A (curve 1) and of element B (curve 2), when the adsorption frequency of the other element retains the value v=10 τ^{-1} , T=650K, ΔE =1eV, Θ_{4}^{+} =0.5.

frequency of the other element retains the value $v=10\tau^{-1}$, is presented in Fig.4. The growth per cycle increases rapidly with the adsorption frequency of A atoms as far as a considerable difference of the surface coverage from the zero-coverage is achieved during the time corresponding to the maximum growth per cycle. The increase of the adsorption rate of B atoms causes rapid increase of the growth per cycle, when the surface coverage Θ_A , achieved during the time corresponding to the maximum growth per cycle, when the surface coverage Θ_A , achieved during the time corresponding to the maximum growth per cycle, exceeds the zero-coverage. The following increase of the growth per cycle is limited by the lack of suitable adsorption sites in the case, when the adsorption frequency of A atoms increases, and by the abrupt increase of the desorption rate of B atoms, when the surface coverage obtains smaller values than the zero-coverage in the case of increasing adsorption frequency of B atoms. The slow rise of the both curves in the case



Fig.5. The dependence of A (a) and B (b) pulse times corresponding to the maximum growth per cycle, on the adsorption frequency. $1 - v_A$ is changed and $v_B = 10\tau^{-1}$; $2 - v_B$ is changed and $v_A = 10\tau^{-1}$. T=650K, $\Delta E = 1$ eV, $\Theta_A^* = 0.5$.



Fig.6. The dependence of the maximum growth per cycle on the pause time, when the pause follows A pulse (curve 1), B pulse (curve 2) or the both pulses (curve 3). The pause time is measured as the ratio to the B pulse time corresponding to the maximum growth per cycle without pauses. T=650K, $\Delta E = 1eV$, $v_A = v_B = 10\tau^{-1}$.

of high adsorption frequencies is caused by the decrease of the desorption of the other component during the pulse of the first component with increasing adsorption frequency. Consequently, the beam flux increase is reasonable to some extent only, the following change of the adsorption frequencies cannot give considerable increase in the growth rate.

The dependence of the pulse times, corresponding to the maximum growth per cycle, on the adsorption frequencies is presented in Fig.5. Comparison of the deposition times of different components suggests that in the case of the equal adsorption frequencies the time corresponding to the maximum growth per cycle is for B about one order of magnitude smaller than for A. However, in experiments equal pulse times are often used. Here it must be taken into account that, as described above, noticeable decrease of the deposition time of A atoms, compared with that corresponding to the maximum growth per cycle, has not any critical influence on the growth per cycle. At the same time in the case of equal beam fluxes impinging on the surface, evidently the adsorption frequency of B atoms is remarkably less than that of A atoms because the adsorption of B atoms needs the dissociation of the molecules impinging on the substrate.

The effect of the pause time between the pulses on the growth per cycle is investigated. The dependence of the growth per cycle on the pause time after one or the both pulses is presented in Fig.6. During the pause after A pulse the preliminary decrease rate of the layer is about

$$d\kappa / dt = -\lambda_A \Theta_A \tag{3}$$

and in the case of high adsorption frequencies

$$d\kappa / dt = -\lambda_A. \tag{4}$$

The decrease rate of the film obtains the value $-\lambda_A$ since the zero-coverage is achieved during the pause. Thus the decrease of the layer during the pause after A pulse is approximately linear. The pause after B pulse begins with rapid desorption of B atoms, the decrease rate exceeds the value λ_A during the pause until the surface coverage obtains the value equal to the zero-coverage. Thus the pause time after B pulse has greater effect to the growth rate. It must be mentioned that the pause between the pulses cannot change the behaviour of the dependences of the growth on adsorption frequencies and pulse times presented above.

In this paper the relationships between the parameters determining the film growth and the effect of the choice of the values of these parameters on the growth of binary compounds during ALE MBE are presented. The choice of the values of the parameters for specific materials is possible, if the dependence of the zero-coverage and the desorption frequencies of the components on temperature and the difference between the desorption energies of nonmetallic atoms, corresponding to different zero-coverages, are determined by experiments independent of the film growth.

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GROWTH RATE AND SOURCE MATERIAL UTILIZATION EFFICIENCY IN MBE UNDER CONVENTIONAL AND ALE CONDITIONS

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Abstract

A model based on kinetic equations describing the adsorption and desorption balance is used to estimate the growth rate and the source material utilization efficiency in the case of MBE under conventional and ALE conditions. Comparative analysis of these growth conditions is carried out.

Introduction

Atomic layer epitaxy (ALE) [1,2] has been demonstrated to be an attractive technique for thin film growth. Until now this mode of crystal growth has been realized by means of molecular beam epitaxy (MBE), chemical vapor deposition and liquid phase epitaxy. By this method layers as thin as one atomic layer with extreme uniformity can be formed. However, the conventional growth techniques, where the different constituents of the binary compound are deposited simultaneously, should have advantages in the growth rate and in the source material utilization efficiency. Thus, to choose the optimum growth mode, comparative analysis is inevitable.

The formulae for calculation of the binary compound growth rate in the case of conventional MBE [3] and the surface coverage dynamics in the case of ALE [4–7] have been derived previously. Formulae for the ALE growth rate have been presented for the case when the desorption rate is averaged over the pulse and purge times [8]. However, the variation of the desorption rate during one ALE cycle has a significant effect on the growth rate. Complete formulae for the characterization of a single ALE step as well as conventional MBE, have been derived in [9]. On the basis of these formulae rules for calculating the rate of cyclic growth have been presented [10,11]. In the present work we apply these rules to compare the growth rate and the material utilization efficiency corresponding to ALE with those corresponding to the conventional MBE in similar conditions, provided that the elemental sources A and B are used for the growth of AB compound.

Results and discussion

Assuming that the adsorption frequencies v_A and v_B of A and B atoms, respectively, are constant during deposition and the desorption frequencies λ_A and λ_B of A and B atoms are constant during the growth process, one can present the changes of the numbers of A and B atomic layers in the film during one growth step or during conventional MBE [9] as

$$\Delta \kappa_{i}(\tau) = \kappa_{i}(\tau) - \kappa_{i}(0) = \frac{v_{h}v_{b} - \lambda_{h}\lambda_{b}}{\lambda} \tau + \left[\frac{v_{i} + \lambda_{j}}{\lambda} - \Theta_{i}(0)\right]\frac{v_{i} - \lambda_{i}}{\lambda} \left[1 - \exp\left(-\lambda\tau\right)\right]$$
(1)

where t is time, Θ_{i} is the surface coverage with i atoms, i, j=A,B, i=j and

$$\lambda = \lambda_A + \lambda_B + \nu_A + \nu_B. \tag{2}$$



Fig.1. Thickness of the film grown under conventional and ALE conditions, versus the growth time t. $v_A = 20\tau^{-1}$, $v_B = 4\tau^{-1}$, $\Theta_A(0) = 0$.

- the change of A atomic layers

Eq.1 enable us to deduce the growth rates

$$G_i = d\kappa_i / dt \tag{3}$$

as well as the constituent elements utilization efficiencies defined in this work as

$$\eta_I = [\kappa_I(\tau_2) - \kappa_I(\tau_1)]_I \int_{-\infty}^{\infty} v_I dt .$$
(4)

Under the conventional conditions at $t >> 1/\lambda$ we get a formula for the growth rate identical with that of Yao and Maekawa [3]. Under ALF conditions the growth process includes the exposure of the surface to the alternating pulses of elements A and B with the pulse durations t_A^+ and t_B^+ , each of them followed by the pauses with durations t_A^- and t_B^- respectively (Fig.1). Consequently, the parameters averaged over the complete ALE cycle have to be used for the characterization of the cyclic growth



Fig.2. The growth rate G of the film under conventional (----) and ALE (-----) conditions as a function of the adsorption frequency $v = v_A = v_B$ at various exposition times $1^+ = t_A^+ = t_B^+ = 0$.

The number of deposited atomic layers as a function of growth time is shown in Fig.1. The calculations were carried out assuming that $\lambda_A = \lambda_B$ and $\Theta_A = 0$ at t=0. The time unit was chosen equal to the reciprocal desorption frequency $1/\lambda_A$. As one can predict, the film grows monotonously in the case of conventional MBE. The curves corresponding to different elements do not coincide because the initial surface coverage is not equal to the one established during the growth. G_A and G_B obtain equal values when the equilibrium between solid surface and molecular beams is achieved. When the initial surface coverage value is the equilibrium one, the curves G_A and G_B coincide.



Fig.3. Constituent element A utilization efficiency η_A as a function of the adsorption frequency $v_A = v_B$ at various pulse times $t^+=t_A^+=t_B^+$ under conventional (------) and ALE (-----) conditions. $t_A^-=t_B^-=0$.

In the ALE mode the solid is not in balance with a molecular beam. However, constant growth per cycle is obtained after few cycles provided that the beam intensity is high enough. This constant value of G_i as a function of adsorption frequency is shown in Fig.2. The parameter t_m is the pulse time corresponding to the maximum growth per cycle. As shown earlier [10] the growth per cycle increases with the increase of the exposure time at small t_i^+ only, while at high values of t_i^+ it decreases slowly. Calculations show that at $t_i^-=0$ the growth rate G_i decreases with increasing exposure time in the whole range of t_i^+ . In the case when $t_i^->0$ the growth rate has a maximum at a certain value of t_i^+ which, however, does not coincide with t_m . Fig.2 demonstrates that



Fig.4. Constituent element A utilization efficiency η_A versus the adsorption frequency v_A at various ratios of the adsorption frequencies v_B/v_A under conventional (------) and ALE (-----) conditions. In the case of ALE $t_A^+=t_B^+=0.25\tau$, $t_A^-=t_B^-=0$.

the growth rate of conventional MBE exceeds remarkably the growth rate of ALE. This difference increases with the adsorption frequency because in the case of ALE the increase of κ_i during t_i^+ cannot exceed the difference between the equilibrium surface coverage under corresponding molecular beam and the surface coverage obtained before this exposure. At high adsorption frequencies when the coverage obtains equilibrium value during the pulse time, the additional increase of v_i has no effect on the cyclic growth rate.

Fig. 3 and 4 present the source material utilization efficiency as a function of adsorption frequency. In Fig.3 the adsorption frequencies of different elements are chosen equal one to the other and different curves of ALE correspond to different pulse times. As one can see, η_i depends nonmonotonously on the adsorption frequency. Relatively stable utilization efficiency is inherent to the curve corresponding to the maximum growth per cycle. The utilization efficiency of the source materials in ALE is noticeably lower than in conventional MBE. Fig.4, where different curves correspond to different ratios of the adsorption frequencies of the components, indicates that the utilization efficiency of one constituent element can be increased at the expence of another, under conventional as well as under ALE conditions. At high values of v_A such effect is smaller in the ALE mode and hence, the growth is more stable than in the conventional mode. At the same time the values of G_i and η_i under conventional conditions exceed considerably those corresponding to ALE conditions. Therefore our calculations confirm that the advantages of ALE mode are mostly obtained at the expence of growth rate and source material utilization efficiency. The calculations also demonstrate that one can optimize the conditions for the ALE growth to obtain maximum growth per cycle. maximum growth rate or maximum source material utilization efficiency However, in general case the conditions can not be optimized for two or more of these quantities simultaneously

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INVESTIGATION OF SrS-Ce PHOTOLUMINESCENCE EXCITED BY SHORT PULSES

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Abstract

The photoluminescence of SrS and SrS-Cc phosphors caused by steady-state and impulse excitation was investigated. It was established that in the case of impulse excitation (E_{exc} =3.68 eV) in the luminescence spectrum of SrS-Ce in addition to the well-known radiation bands originated by the Ce³⁺ ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$. ${}^{2}F_{7/2}$ transitions with quantum energy about 2.31 and 2.57 eV, two new bands appear, with their maximums at 2.72 and 3.15 eV (300 K) or 2.77 and 3.21 eV (80 K) correspondingly. We suppose, that these radiation bands are caused by a free electron and/or the trapped electron (situated on a low traps) recombining on the Ce³⁺ centers in the SrS lattice are not similar for all the centers.

Introduction

The sulfides of alkaline earth chalogenides, among them SrS. have for years been of interest for the scientists. This is due to various applications for the representatives of this compound. Let us mention here the classical applications in dosimetry [1,2] and in electron ray tubes (the source of the cathodoluminescence) [3,4]. During the last few years these materials have become more popular yet, thanks to the new-found possibility to apply them as active materials in production of the thin film electroluminescent panels. It should be noted that SrS-Ce is considered a very promising active layer material for blue electroluminescent films [5,6], and SrS-Ce. K. Eu and SrS-Pr. K are hoped to become active layer materials for white-light and full-color thin film electroluminescent panels [7,8].

Although the scientists are greatly interested in these new materials, the electronical processes taking place in them are, to a great extent, unknown. The main aim of the present paper is to investigate the electronical processes taking place in SrS-Ce via measurements of the photoluminescence, caused by relatively short (10 ns) optical (E_{exc} =3.08 eV) impulses with high excitation power density (50 kW/cm²).

Experimental

The host material, SrS, has been synthesized at the Anorganic Chemistry Department of Tartu University. The method used is described in the paper [9]. The SrS:Ce phosphors under investigation in the present paper were prepared by firing the SrS powder mixed with Ce₂(SO₄)₃*8H₂O, KCl and 3 at 1100 °C. The concentration of Ce in the phosphors under investigation was 0, 0.316, 1.0, 3.16 and 5.0 mol%.



Fig.1. Experimental arrangement used to record the photoluminescence relaxation and spectra.

1-laser LGI-21; 2-semitransparent mirror; 3-lens; 4-phosphors in cryostat; 5-lens; 6semiconductor diode with amplifier; 7-optical filter BS-8; 8-doublemonochromator MDR-6; 9-photoelectric multiplier FEU-87; 10-time delay circuit; 11-sampling converter V9-5; 12-former of synchronizing pulse; 13-CAMAC controller; 14-analogdigital converter: 15-digital-analog converter; 16-input register; 17-step motor controller; 18-personal computer AT286; 19-printer. The principal scheme of the equipment used to measure the photoluminescence of phosphors excited by short radiation impulses is presented in Fig.1. The radiation source (quantum energy $E_{exc}=3.68 \text{ eV}$) was the nitrogen laser LGI-21 (1), with impulse duration of 10 ns (at their half height) and frequency of 10 Hz. The impulse, with energy about 30 μ J, creates after passing through the optical system the density of the radiation flow about 50 kW/cm² on the sample surface in the area with its perimeter equal to 1 mm.

The phosphors were pressed into the corresponding indents of the cold finger of the cryostat (4). The phosphors in the cryostat were investigated at the room temperature (300 K) and during cooling with the help of liquid nitrogen (80 K).

The emission was analyzed with a double monochromator MDR-6 (8) and detected with a photomultiplier FEU-87 (9). The electrical signal of the latter was measured by a sampling converter V9-5 (11), the time resolution of which is 4 ns. The synchronization of the sampling converter with the laser was realized by the signal created on the photodiode by the excitation radiation impulse. The necessary delay of the useful signal was created with the help of the time delay circuit (10).

To control the monochromator and the sampling converter and to store the data CAMAC-system (13-17), directed by a personal computer (18), was used.

The analog signal from the sampling converter was transformed to digital form by the analog-digital converter (14). The analog-digital converter was synchronized with the sampling converter by the impulse former (12), driven by signal from the latter. The scanning in the time scale of the sampling converter was realized by the digital-analog converter (15). The scanning of the monochromator in the range of possible wavelengths was realized by the CAMAC-module MUSD (17), the feedback- via module MOD-1 (16).

The data gathering by the system CAMAC, storage and processing, also the printing of necessary results were computer controlled.

To carry out steady-state photoluminescence spectra measurements, the equipment described above had to be slightly modified. For the radiation source a low pressure Hg lamp PRK-7 was used. The excitation radiation (E_{exc} =3.96 eV) was separated out by a filter UFS-2 and a liquid filter, filled with water solution of NiSO₄. The time delay circuit and sampling converter were replaced by the current amplifier. The output of the latter was coupled with the input of the analog- digital converter (14). There was no need for the synchronization devices and digital-analog converter in this case.

Experimental results

In the spectra of SrS-Ce phosphors under investigation in the case of steadystate excitation the well-known radiation bands with their maximums of 2.31 (2.31)¹ and 2.57 (2.58) eV dominated. These maximums are considered [10–12] due to transitions

¹In brackets we give the value of the corresponding parameter at 80 K temperature


Fig.2. SrS-Ce (3.16 mol%) luminescence spectra at 300 K. a) Luminescence spectra in the case of steady-state (3) and impulse excitation (1,2). The spectra 1 and 2 have been measured 14 and 85 ns after the excitation impulse maximum. b) Luminescence bands (1-3) calculated for the measured spectra (a) using the method described in [13].



Fig.3. StS=Ce $_{13}$ 10 mol(α) luminescence spectra at 80 K. a) Luminescence spectra in the case of steady-state (3) and impulse excitation (1,2). The spectra L and 2 have been measured 23 and 53 ns after the excitation impulse maximum b) Luminescence bands (1-2) calculated for the measured spectra (a) using the method described in [13]



Fig.4. Time dependence of the SrS-Ce (0.316 mol%) luminescence at 300 K (a) and 80 K (b), with quantum energy of 3.10 eV (1) and 2.61 eV (2).

 ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ in Ce³⁺ (curve 3 on Fig.2a and 3a). At the 80 K temperature the intensity of luminescence overreached the level of the intensity at room temperature about 2-3 times. In the range of short wavelengths (E > 2.8 eV) in the case of steady-state excitation we registrated a weak luminescence only, with its maximum at about 3.1 eV. The luminescence of the phosphors without the Ce-activator was one of the weakest among the phosphors investigated. The only radiation band of this phosphor we detected had its maximum at 2.35 (2.49) eV. Among the phosphors investigated the most efficient appear the phosphor with the Ce-content of 0.316 mol%. This phosphor remained the most efficient in the case of impulse excitation too. The luminescence intensity of SrS-Ce (5.0 mol%) is noticeable weaker than that of SrS-Ce (0.316 mol%).

Curve 1 and 2 on Fig.2a and 3a represent the photoluminescence spectra, measured in the time interval from 3 to 75 ns after the maximum of the excitation impulse. The main difference of the photoluminescence spectrum produced by the impulse excitation from the spectrum produced by steady-state excitation consists in domination of the new shortwave bands in the initial phase of the photoluminescence response. In the phosphors under investigation the maximal intensity of these bands lies in a quite good correlation with the intensities of the Ce³⁺ (${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$) bands measured under steady-state excitation. They had their maximal intensity in the case of the SrS-Ce (0.316 mol%) phosphor and they were undetectable for us in the SrSphosphor, where the Ce-activator was absent. These bands were also very difficult to detect in the phosphor SrS-Ce (5 mol%), where the intensity of the bands determined by the Ce³⁺ centre transitions ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ is small too.

In Fig.4a and 4b the time dependence of the photoluminescence intensity in the case of the luminescence quantum energy equal to 3.10 and 2.61 eV at temperatures 300 and 80 K is presented. We can see that the increase of the photoluminescence up to its maximal value is 3-5 (5-7) ns quicker for the quantum energy of 3.10 eV in comparison with 2.61 eV. Similarly the time factor characterizing the decrease in the intensity of the photoluminescence at the quantum energy of 3.10 eV equals to 35 (30) ns, the relaxation time factor characterizing the transitions of Ce³⁺ centre equals to 55 (50) ns.

Discussion

In the photoluminescence spectra created by impulse excitation noticeable coverage of the spectral bands originating from $Ce^{3+}{}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ transitions by the bands originating from the high excitation density takes place. To establish the shape of both bands in this spectrum we used the method for separation of the individual bands described in [13]. For calculation we used the spectra measured at different moments after the excitation impulse maximum e.g. the curves 1 and 2 in the Fig.2a and 3a. The method [13] is in this situation very convenient, as the curve describing the ratio of the spectra, measured at different moments, has the plateau in the range of short wavelengths as well as of long wavelengths. In Fig.2b and 3b the individual spectral bands, obtained

using this method, are presented. It is evident, that we have reach the individual spectral bands (2), corresponding to the ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ transition of Cc³⁺ ion, which with high precision coincide with the spectral bands measured in the case of the steady-state excitation (curve 3 in Fig.2a and 3a).

In the spectra measured at with high excitation density we can distinguish first of all two luminescence bands with maximums at 2.73 (2.77) and 3.15 (3.21) eV (curve 1 in Fig.2b and 3b). It is remarkable that in the time interval investigated by us (at least 100 ns), the change in the intensity ratio and position of the luminescence band maximums could not be detected. The investigation of the photoluminescence of SrS phosphors with different Cc concentrations seems to ascertain that the above-mentioned shortwave radiation is related (in direct or indirect way) to the concentration of Ce3+ ions available for luminescence transitions. The positions of the maximums of these radiation spectra behave differently from the spectra of the radiation caused by the intracenter transitions ${}^{2}T_{2\sigma} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$. The former deviate at lower temperatures towards the quantums with greater energy. This fact proves that in the generation of the above-mentioned shortwave luminescence bands the free carrier and/or the trapped carrier from shallow traps take part in. The appearance of free electrons on the excitation wavelength is energetically possible, as the distance of the Ce³⁺ ²F_{5/2} niveau from the minimum X₃ of the conductive band [12,14,15] is less than the quantum energy of the nitrogen laser radiation. The appearance of free charge carriers in the process of the Ce3+ ion excitation has been described in the earlier publications [8,16,17].

In the phosphors investigated by us the $Ce^{3+} {}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$ band intensity decreases not exponentially (Fig.4a and 4b). This fact also suggest that in the excitation process electrons are released.

According to the data available it is possible to suppose that the radiation bands that appear at high excitation densities could be caused by the recombination of free electrons or/and the electrons trapped by shallow donors with Ce^{4+} ion.

It is inevitable to continue with experiments to make more clear the nature of the transitions causing the existence of the corresponding luminescence bands.

In addition to the two luminescence bands described in previous paragraphs, the application of the method described in [13] helped to detect a radiation band with its maximum near 3.25 eV (curve 3 on Fig.2b). This band was apparent at the room temperature only, and it vanished in less than 70 ns.

We should like to point out, that the measurements realized on the high excitation level show, that there are Ce-centers in existence in SrS-Ce, which differ one from another in characteristics of their surroundings. This fact is ascertained by the dependence of the radiation spectra ratio on the wavelength at 80 K. If the ratio is calculated for the spectrum which is measured at the moment of maximum of the luminescence and the luminescence spectrum measured at any other moment, then the dependence of the ratio on wavelength has its maximums on the quantum energy 2.31and 2.57 eV. If the spectrum with the highest intensity is not used, the plateau is situated in the same region. So we can conclude that at high excitation densities the luminescence centers with radiation bands somewhat different from usual Ce³⁺ radiation bands ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ take part in the luminescence. Evidently the relaxation time of these luminescence centers is very short.

Conclusions

As the result of the impulse excitation (E_{exc} =3.68 eV, ~50 kW/cm²) in the luminescence spectrum of SrS-Ce in addition to the radiation bands, with their maximums at 2.31 (2.31) and 2.57 (2.58) eV, caused by the transitions of Ce³⁺ centers ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ the new radiation bands with maximums at 2.73 (2.77), 3.15 (3.21) and 3.25 eV will appear.

The intensity ratio and position of luminescence band maximums of the two first mentioned new radiation bands does not have any noticeable change in the decaying process (with durance up to 100 ns), but the third band vanish during the first 70 ns.

The maximum of the luminescence is achieved by the new bands 3-5 (5-7) ns carlier than by the Ce³⁺ centre ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ bands.

The decrease of the luminescence of these bands (the first 30-110 ns) is characterized by the time factor of 35 (30) ns which is shorter than the time factor characterizing the Ce³⁺ centre ${}^{2}T_{2g} \rightarrow {}^{2}F_{5/2}$, ${}^{2}F_{7/2}$ transition bands for the same phosphors.

For the phosphors investigated the intensity of the new luminescence bands correlates with the intensities of the bands related to the transitions of Ce^{3+} centers.

We suppose, that the luminescence radiation bands with their maximums at 2.73 (2.77) and 3.15 (3.21) eV are related with the recombination of a free electron and/or an electron trapped on a low traps with a Ce^{4+} ion.

The data have been achieved, which show that the nearest environment of the Ce^{3+} centers is not uniform in the SrS lattice for all centers.

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