PRODUCTION OF THIN LUMINESCENT FILMS BY CHEMICAL AEROSOL DEPOSITION TECHNOLOGY (CADT).

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Abstract

CADT is used to produce thin luminescent films of ZnS by pyrolysis of ZnCl_2 and $\text{CS}(\text{NH}_2)_2$. SEM-photography and X-ray diffraction studies revealed that under specific experimental conditions polycrystalline ZnS (relative density $\approx 80\%$) with a preferential orientation of the c-axis perpendicular to the substrate was obtained. Luminescence was found in ZnS-films doped with proper amounts of Cu and Al. The luminescence yield increased with better diffusion conditions during film growth.

Introduction

In comparison with other coating techniques like sputtering, evaporation and CVD the Chemical Aerosol Deposition Technology (CADT, often named spray pyrolysis) is a low-cost technique for coating large areas. It is based on the pyrolysis of an aerosol [1,2,3], consisting of small droplets of a solution which contains the precursor compounds. The aerosol, produced for example by ultrasonic spraying of this solution, is transported to a heated substrate by a carrier gas. As a consequence of the increased substrate temperature the aerosol particles will pass through a traject of continuously rising temperature, resulting in a gradual change of their chemical composition [1]. Fig.1. shows several possible decomposition modes in relation to the substrate temperature. The microstructure of the film and hence its physical properties strongly depend on which decomposition mode is used. It is emphasized that the substrate temperature defines both the decomposition mode and the diffusion conditions during film growth.

Fig.1. Decomposition modes. The phase of the particles, reaching the substrate is presented.

In order to obtain an appropriate luminescence it is necessary to produce a film having a crystalline structure and a high relative density. The best way to meet these requirements would be to produce films under the conditions for CVD (mode 4, fig.1., [4]). The optimal process conditions are determined by experiments with pure ZnS and are applied in experiments with doped ZnS.

Preparation and structural characterization of the films

A schematic view and some relevant geometrical dimensions of the aerosol set-up we have used is given in fig.2. The set-up is mounted in a so-called laminar flow box in order to avoid interference from dust particles. An ultrasonic spray unit, which uses a frequency of 3 MHz, is able to generate aerosol particles (droplets) having an average diameter of $2\ \mu\text{m}$ [1]. The impactor acts as a filter for eliminating large particles by centrifugal force. The (computer controlled) translation stage may be moved with regular patterns in order to create a film of equal thickness over the entire substrate surface. In our case we have not used this option.

Fig.2. Aerosol set-up.

Thin films of ZnS were produced by spraying 100 ml of a solution of 0.1 M ZnCl_2 and 0.1 M $\text{CS}(\text{NH}_2)_2$ in methanol on a glass substrate held at a temperature of 500 °C. To prevent the formation of oxides, nitrogen was used as carrier gas with a flow rate of 3 l/min. SEM-photography revealed that the morphology of the film varies with the position on the substrate. In regions near by the nozzle a thin film showing a pancake-like structure was observed (fig.3a.). In regions further away from the nozzle a thicker film consisting

Fig.3a. SEM-photograph (20.000x) of a region near by the nozzle.

Fig.3b. SEM-photograph (20.000x) of a region away from the nozzle.

of a large amount of distinct columns growing from a thin initial layer was observed (fig.3b). X-ray diffraction showed that in all regions polycrystalline ZnS (mainly hexagonal; α -ZnS) was formed, the columnar structure showing a pronounced preferential orientation of the c-axis perpendicular to the substrate. The film density (about 20 %) and the deposition efficiency of both microstructures were low.

Discussion and further experiments

We ascribe the columnar structure to a CVD-like reaction (mode 4). The columns are built up atomically from the gas phase. This occurs very gradually allowing the formed ZnS to adapt, by surface diffusion, the existing crystal

structure. The low deposition efficiency in the CVD-mode arises from thermodiffusion of the gaseous compounds away from the hot surface. The low density of this structure may originate from either a lack of properly oriented nuclei in the initial layer or from poor kinetics in a later stage of film growth. To make this clear we reproduced the experiment but now using a glass substrate coated with a thin (0.2 μm) sputtered ZnO-layer, thus providing epitaxial growth conditions: the crystallographic parameters of ZnS and ZnO closely resemble each other; these ZnO-films show a very dense columnar structure with a pronounced preferential orientation of the c-axis perpendicular to the substrate [5]. The structure of the ZnS film, obtained in this way, is depicted in fig.4. The film density was greatly increased so we can conclude that a lack of properly oriented nuclei contributes considerably to the low density. Further research concerning initial nucleation is in progress.

Fig.4. SEM-photograph (20.000x) of a ZnS-film on a ZnO-initial layer.

Fig.5. SEM-photograph (20.000x) of a ZnS-film produced by corona-aided CVD.

In our opinion the disordered pancake structure mainly arises from film growth in the spray region (mode 2-4), originating from some large aerosol particles. These particles impinge upon the substrate because they are too large to evaporate in the temperature gradient. Impinging upon the hot surface a large amount of ZnS is directly formed, excluding adaptation of the fresh material, by surface diffusion, to the existing structure. Without further dilution of the spray solution in the spray region a gradual, surface-diffusion limited growth of ZnS from the large amount of small particles on the hot substrate is obtainable. By charging the particles using a corona discharge (corona-aided CVD) they can be accelerated by electric fields into the direction of the hot substrate, rapidly passing through the hot temperature region and so avoiding complete evaporation. In electrical parameters such as charging voltage we find, besides the carrier gas flow rate, an extra degree of freedom to adjust the time the particles spend in the hot temperature region. The final result is an enhanced deposition efficiency [6] and a higher density ($\approx 80\%$) of the ZnS-film. This is illustrated in fig.5.

Corona-aided CVD is used to produce luminescent ZnS:Cu,Al films. The solution of 0.1 M ZnCl_2 and 0.1 M $\text{CS}(\text{NH}_2)_2$ in methanol was therefore enriched with CuCl_2 ($1.5 \cdot 10^{-4}$ M) and AlCl_3 ($3 \cdot 10^{-4}$ M). Substrate temperatures were chosen in the range 400 - 600 $^\circ\text{C}$. SEM-photography and X-ray diffraction showed no morphological and crystallographic changes in the microstructure of the films (with $T_s \geq 500$ $^\circ\text{C}$) compared to the pure ZnS-films. With increasing substrate temperature, the preferential orientation perpendicular to the substrate appeared to be more pronounced, thus indicating an increased crystallographic perfection arising from the higher surface mobility of the atoms during film growth. Cathode luminescence was obtained by excitation of the phosphor with high-energetic electrons (25 keV) resulting into an emission spectrum with maximum intensity at a wavelength of $\lambda = 525$ nm, just as in ZnS:Cu,Al phosphors produced with other technologies [7]. It appeared that only films produced at substrate temperatures ≥ 500 $^\circ\text{C}$ showed luminescence of which the intensity increased with rising temperature. This can be explained by a diminution of the amount of quenching centres which is correlated to the increased crystallographic perfection. The luminescence yield is measured

relative to the reference phosphor P20 (ZnCdS:Ag, $\lambda_{\text{emission}} = 560 \text{ nm}$) and is found to be approximately 23 % at 600 °C. This can be explained by the spectral difference between both phosphors, a deviating concentration ratio of the dope and an insufficient film thickness. Research is in progress to increase this yield.

Conclusions

Thin films of polycrystalline, mainly hexagonal, α -ZnS can be produced by CADT from a solution of ZnCl_2 and $\text{CS}(\text{NH}_2)_2$ in methanol. Dependent on the experimental conditions, spray-region deposition or CVD-like deposition can be realized, the first resulting in a pancake-like morphology the latter into a column-like morphology. The density of the films and the deposition efficiency can be increased by applying corona-aided CADT at substrate temperatures in the range 500 - 600 °C. Luminescent films are obtained by codoping with Cu and Al. The films show the common ZnS:Cu,Al emission spectrum. Their yield is still remarkably smaller than the yield of the commercial phosphor ZnCdS:Ag.

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