

Microstructure and related properties of obliquely deposited AgCl thin films*

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Thin films of crystalline silver chloride are deposited under high vacuum conditions via thermal evaporation of pure AgCl onto pre-cleaned soda-lime glass substrates. A grain-like surface structure and columnar growth morphology are visualized by means of a scanning electron microscope. The increase of the vapour incidence angle α is accompanied with a rise in the film porosity and roughening of the sample's surface structure. As a result, the microhardness, DC conductivity and the refractive index of the obliquely deposited AgCl thin films decrease abruptly at $\alpha > 50^\circ$. The measured efficiency for the detection of humidity or reactive vapours, such as ammonia and dimethylamine, demonstrate that the relative sensitivity of the obliquely deposited AgCl films is several times higher, as compared to the samples obtained at normal vapour incidence.

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1. Introduction

The physical properties of silver halides are very suitable for the monitoring of different hazardous gases such as halogens, ammonia, nitrogen oxides, cyan etc. Usually, the electrical resistance is selected as the sensing parameter, which depends on the gas ambient conditions. The observed sensitivity response substantially increases in thin halide films, due to the higher conductivity in the vicinity of the surface, as compared to the bulk. This enhanced surface conductivity is controlled by the ionic space charge from silver ion interstitials accumulated in the subsurface region of AgBr, AgCl and AgI [1].

Among the different silver halides, AgCl thin films are the most intensively studied as promising functional materials for the development of a new generation of gas sensors [2-4]. A substantial rise in the AgCl DC-conductivity is observed in an atmosphere with some amount of ionophilic gases such as chlorine, hydrogen sulphide [3], ammonia and cyan [4]. However, the doping of AgCl with Pd and Cd, as well as bilayer AgCl: β -Al₂O₃ [3] or composite AgCl/ α -Al₂O₃ films [4], is necessary for the improvement of the sensor characteristics. It is assumed that the modified composition of AgCl films

results in an increased gas adsorption on grain boundaries, due to the rise in the adsorption centers' number. A similar effect could be realized when the microstructure instead of the composition of the AgCl film is modified, in order to achieve a high surface-to-volume ratio. There is a simple and elegant method for the deposition of "ad initium" porous thin films with a large specific surface and consequently a high concentration of surface centers responsible for gas adsorption. This is based on oblique thin film deposition using collimated vapour flux orientated under a definite angle towards the substrate normal.

The present paper aims to study the influence of the oblique vapour deposition on the microstructure, electrical and sensing properties of thin AgCl films.

2. Experimental

The AgCl samples are deposited under high vacuum, better than $5 \cdot 10^{-4}$ Pa. An indirectly heated Pt crucible mounted in a water cooled massive silver block is used as a vapor source. This reveals the possibility to maintain precisely the temperature of the melted AgCl – a high purity material (99,99999%), the deposition rate being 0,5

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nm/s. The substrates, pre-cleaned soda-lime glass plates at room temperature, are positioned at different vapor incidence angles α between the substrate normal and the crucible axis. Thus, α is changed from 0° to 75° , and 2 - 3 μm thick films are prepared by only varying the deposition time.

The microstructure and growth morphology of the AgCl films are inspected under a scanning electron microscope (Phillips SEM 515). For growth profile visualization, a microfractographic technique is applied; the details of this preparation procedure being described earlier [5]. Conductive C and Au coatings, about 10 nm thick, are consecutively deposited onto the sample surface, in order to enhance the contrast of the obtained SEM image of the growth profiles. The specific surface is analyzed via BET method, the adsorbent used being krypton gas [6].

As-deposited samples are used for the further study of the mechanical, electrical and optical properties of the AgCl films. All measurements are made in the plane determined by the vapor beam direction and its projection on the substrate surface. The microhardness of the samples is evaluated via Knoop prism indentation, and their refractive index is calculated from the optical transmittance measured by means of a Cary 5E UV-VIS-NIR spectrophotometer. All details of both methods applied are described elsewhere [7].

The DC dark conductivity measurements of the as-deposited samples are made in a direction parallel to the film surface. Narrow Au strip contacts, vacuum deposited on the free AgCl surface, are used. The electrical resistance R of the samples is measured by means of a four-arm Wheatstone bridge, in the temperature range 20° to 100°C , maintained to an accuracy of $\pm 0.5^\circ\text{C}$. As described earlier [1], a specially designed thermostat provides conditions for R -measurement vs. temperature in an inert gas ambient; pure dry nitrogen at atmospheric pressure. Before these measurements, each sample is annealed in the thermostat at 100°C . The experimental set-up provides a high accuracy of the measured resistance, and the maximal error never exceeds 5% in the whole temperature region studied.

The samples' ability for the detection of different vapours is evaluated at room temperature as a relative sensitivity $|S| = [(R_i - R_r)/R_i] \cdot 100\%$ [8], where R_i and R_r are the film resistivity in an inert atmosphere; dry pure nitrogen, or reagent gas respectively. For this purpose, saturated vapours of water, ethanol, ammonia, acetone or dimethylamine are leaked into the evacuated thermostat vessel.

3. Results

The AgCl films deposited at different vapour incidence angles α are polycrystalline, with an orientation

along the [111] axes. The SEM micrographs of the top film surface (Fig. 1.) illustrate the grain-like surface morphology of the samples. The surface microstructure evolution when α rises is accompanied by a grain transformation into polygonized crystallites. The corresponding growth profiles are shown in Fig. 2.

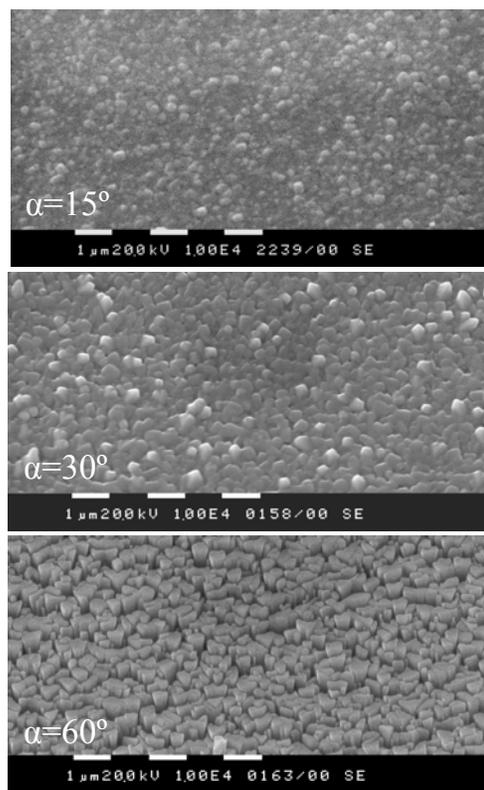


Fig. 1. SEM micrographs of AgCl films deposited at different vapour incidence angles, α .

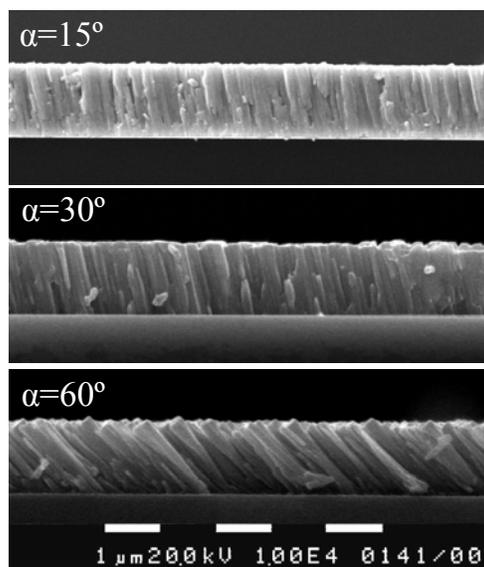


Fig. 2. Growth profiles for films as in Fig. 1.

It is clearly seen that AgCl grows in the form of close packed individual columns running through the entire film thickness. At $\alpha > 50^\circ$, the columns are separated by a free volume in the form of pores. This results in a substantial increase in the film specific surface between 1.4 and 6.8 m^2/g , when α rises from 0° to 60° [9].

The revealed microstructure strongly influences the physical properties of the AgCl films studied. As shown in Figs. 3 and 4, the microhardness M_h and the refractive index n of the samples are dependent upon α , the higher vapour incidence angle, the lower M_h and n . It should be mentioned

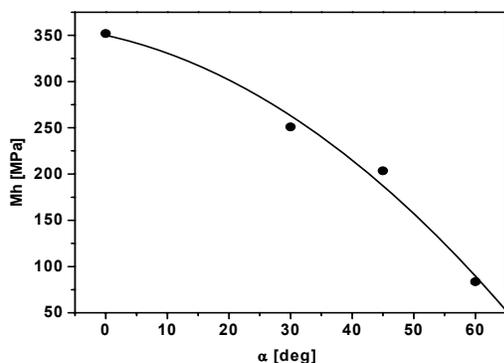


Fig. 3. Microhardness M_h of AgCl films vs. the vapour incidence angle α .

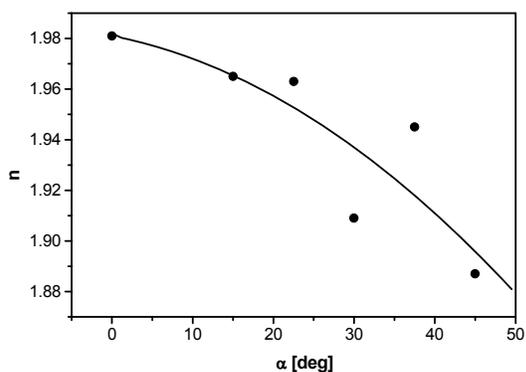


Fig. 4. Refractive index of AgCl films vs. the vapour incidence angle α , calculated for $\lambda=600$ nm.

here, that the refractive index could not be calculated for $\alpha > 50^\circ$, since the films deposited at higher incidence angles are opaque and the optical transmittance drastically decreases, being zero at 60° in the entire visible wavelength range.

Fig. 5. illustrates the DC-conductivity of AgCl films, as dependent on α at room temperature. For simplicity, the σ values are presented per unit area. Comparing the data at $\alpha = 0^\circ$ and $\alpha > 60^\circ$, it is clear that σ decreases by several orders of magnitude at the highest vapour incidence angles. However, the film conductivity has an extremum in the interval $0^\circ < \alpha < 50^\circ$, the maximum σ -value being in the vicinity of $= 30^\circ$.

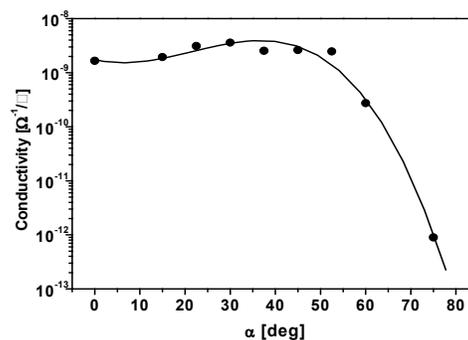


Fig. 5. DC-conductivity σ of AgCl films vs. the vapour incidence angle α for ambient conditions ($t=25^\circ\text{C}$).

Obviously, the conductivity of samples deposited at $\alpha > 60^\circ$ is so low that the AgCl films are not suitable for sensor applications, in spite of their very high specific surface area. Therefore, the relative sensitivity for the detection of different reagents is compared for films deposited at vapour incidence angles of 0° and 60° . The results obtained are summarised in Fig. 6.

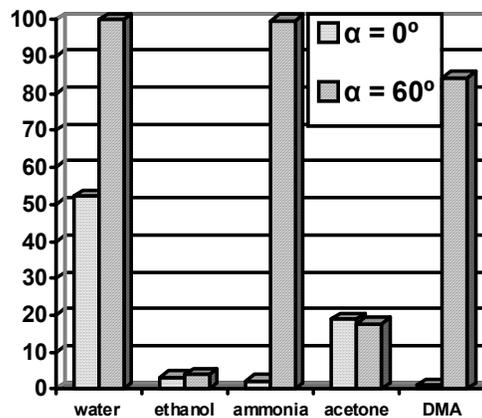


Fig. 6. Relative sensitivity $|S|$ of AgCl films deposited at vapour incidence angles of 0° and 60° in different ambient atmospheres.

4. Discussion

The results obtained demonstrate that the vacuum condensation of AgCl on glass substrates follows some general trends of thin film growth. Both the surface morphology and the internal film structure are strongly influenced by the deposition conditions. The observed grain like microstructure of the AgCl surface results in a columnar growth morphology. As manifested above, the column packing density is very sensitive to the vapour incidence angle and a porous structure with considerable free volume is formed at higher vapour incidence angles $\alpha > 50^\circ$. The evolution of the film microstructure from densely packed to individual-column-arranged, when α rises, initiates a drastic change in the AgCl film properties. The observed decrease of both the microhardness and the refractive index follows the general structure related phenomena accompanying the obliquely vacuum deposition of other inorganic thin films [5,9]. This decrease means that above 15° , the separation of the individual columns forms free volume, thus resulting in porous films' structure.

Fig. 5. shows that σ increases by about a factor of two, at low vapour incidence angles in the interval $0^\circ \leq \alpha \leq 45^\circ$. However, the maximal error from DC-resistance measurements, as mentioned in the experimental section, does not exceed 5%. Obviously, this dependence of σ on α requires a more detailed explanation. It is well established that the DC-conductivity in the subsurface region of AgCl is much higher than that in the volume; the typical value for large single crystals being about $2 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$ [1]. As a result, the total conductivity of AgCl thin films is between 10^{-5} and $10^{-7} \text{ Ohm}^{-1} \text{ cm}^{-1}$ when the film thickness varies from 100 to 10000 nm respectively. These values are comparable with σ measured at $\alpha \leq 45^\circ$. Thus, it is clear that the moderate increase of the film conductivity, when the vapour incidence angle rises from 0° to 45° , is due to the increased surface-to-volume ratio, since the length of the close packed columns increases with α . At higher vapour incidence angles, the individual columns are separated from voids, and the AgCl films are more or less porous. In this case, the charge carrier transport between the columns is impeded and it should occur through a network of intercolumnar electrical contacts, where the charge transfer coefficient is higher.

Finally, the evaluation of the relative sensitivity $|S|$ of the samples in different vapour atmospheres shows that the obliquely deposited AgCl films are very suitable for the detection of humidity, ammonia and DMA. As expected, the sensing efficiency increases abruptly for samples with porous microstructures, which is typical for AgCl deposited at $\alpha \geq 60^\circ$. The S -values measured in saturated ethanol or acetone vapours are below 20%. This means that the threshold concentration of both reagents, as

well as the minimal detectable signal with AgCl films, will tend to zero. A possible explanation of this result is the ionophobic nature of both reagents, which does not interact with the subsurface ionic space charge, and does not influence the electrical transport in the films studied.

5. Conclusion

The present study offers a novel possibility for the preparation of porous thin films as functional materials for sensor techniques. On the basis of long term experience, the authors are convinced that oblique vapour deposition could be used for the improvement of the sensor characteristics of other inorganic and organic thin films.

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