



Laser-induced photodeposition from ZnS colloid solutions

A. Peled^a, B. Dragnea^b, Rodica Alexandrescu^{b,*}, A. Andrei^c

^a *Electrical and Electronics Department, Center for Technological Education Holon, aff. Tel-Aviv University, 52 Golomb St., Holon 58102, Israel*

^b *Institute of Atomic Physics, P.O. Box MG-6, Bucharest, Romania*

^c *Institute for Nuclear Reactors, Pitesti, Romania*

Received 27 May 1994; accepted for publication 20 September 1994

Abstract

The results of ZnS photodeposition from aqueous ZnS colloid solutions by KrF laser irradiation at 248 nm are given. In this process, the photoexcitation of ZnS colloid particles initiates complex redox processes, resulting in simultaneous ZnS thin film photodeposition and Zn particle precipitation in the bulk of the reaction cell. The zinc-based layers, which were deposited onto quartz substrates were investigated by the XPS technique. The dependence of the ZnS film stoichiometry on the initial colloid concentration and its photoactivity was determined.

1. Introduction

Photoassisted processes used to deposit thin films of metals, insulators and semiconductors are an investigation area of current interest [1–2].

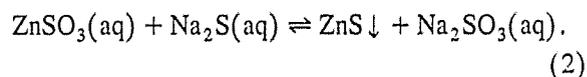
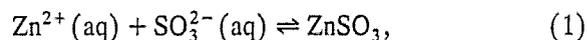
Some successful attempts to obtain photodeposition processes in liquid phases such as from colloid solution [3–5], electrolytes [6], and metallic suspensions [7] using UV or visible light have shown that these techniques can provide some advantages over gas-phase processes. The advantages are higher light energy conversion, due to higher material densities involved, smaller particles diffusion and ease of environmental production. In particular, inorganic colloid solutions have been investigated for their photochemical activity in connection with photodeposition of a-Se films [4] and Cd from CdS colloid

solutions [5]. Gas-phase photodeposition process of Zn [8], ZnSe [9,10] and ZnS [11,12] have already been developed, since thin layers of zinc semiconductor compounds find important optical applications.

In this paper we describe our results on UV laser-induced photodeposition from ZnS colloid solutions, using the techniques developed previously [3–5].

2. Experimental

The ZnS colloid solution was prepared using the technique used for CdS colloids [5]. The dispersion of ZnS/Zn²⁺ was obtained according to the following equations:



* Corresponding author.

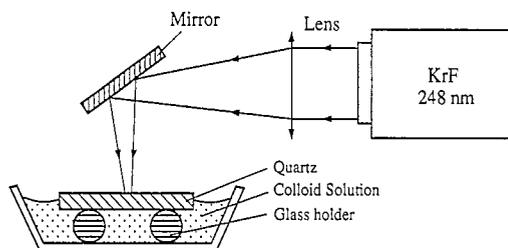


Fig. 1. Schematic representation of the experimental arrangement and of the photodeposition cell used for laser-induced experiments.

The Zn^{2+} aqueous solution is prepared from ZnSO_3 , followed by the precipitation in the dark of ZnS dispersion, in the presence of Na_2S and Na_2SO_3 . The metastable $\text{ZnS}/\text{Zn}^{2+}$ colloid system becomes photoactivated when irradiated with UV light and elementary Zn is precipitated.

During the experiments, the colloid concentration was increased by slightly increasing the content of Na_2S . The irradiation of the metastable sol was conducted in the experimental arrangement shown in Fig. 1. A quartz plate was immersed on one side in the colloid solution, while from the other side it was irradiated by the UV radiation of 248 nm derived from a KrF excimer laser. The laser was operated at a frequency of 1 Hz, 10 ns pulse duration and 60 mJ delivered per pulse. The optical transmissions of the ZnS colloid solution and of the deposited films were spectrophotometrically monitored in the UV and IR spectral regions, respectively. The composition of ZnS photodeposited films was analyzed by X-ray photoelectron spectroscopy (XPS). The photoelectron spectra were obtained with a VG ESCALAB MK II system (at a pressure of 9×10^{-10} mbar). The $\text{AlK}\alpha$ exciting radiation was employed. The calibration of the spectra was performed using the $\text{Ag}3d_{5/2}$ ($h\nu = 368.26$ eV) and $\text{Ag}M_4\text{NN}$ ($h\nu = 1128.78$ eV) lines, with the Fermi level as an energy reference. The spectra of $\text{Zn}2p$, $\text{S}2p$, $\text{O}1s$ and $\text{Si}2p$ were recorded. A 'flood gun' was used to correct for charging effects and the location of $\text{C}1s$ at 284.5 eV, from the carbonaceous surface contaminant, was taken as a reference for calibrating the different spectra. Following the experimental procedure described above, thin films were deposited on quartz substrates by laser irradiation of $\text{ZnS}/\text{Zn}^{2+}$ colloid solutions. It was observed that due to an incubation

period described previously [5], the threshold laser energy dose needed to obtain a compact thin layer was approximately 3000 pulses. During the photodeposition experiments, the color of the colloid solution turned into light-brown, indicating that a simultaneous volume photodeposition (VP) effect occurs. Scanning electron microscopy showed that the films deposited from the irradiated ZnS colloid solution had a smooth and homogeneous surface and reproduced the shape of the laser spot. Typical depositions were performed at a fixed number of laser pulses ($N = 3600$). With higher doses, i.e. $N > 3600$ the adhesion diminished and the films peeled off with time.

The film thickness was calculated from IR transmission measurements calibrated by an interference microscopy method [13]. For a variation of laser pulses in the range $N = 1000 - 3600$, the film thicknesses obtained were between 100 and 600 Å.

3. XPS analysis

The composition of the deposited films, as determined by XPS technique, showed varying concentrations of Zn and S, and also some impurities of O, Si and C. The data were obtained for samples exposed to air, so that the analysis should account for oxygen and carbon contaminants due to post-reactions of the films with the air. Si was detected in the early stages of deposition from the underlying quartz substrate due to incomplete ZnS layer deposition.

The results of an XPS quantitative analysis of the surface photodeposited ZnS layers, deposited from various concentrations of ZnS colloid sols are given in Fig. 2. The films were obtained by irradiating colloid systems with increasing amounts of 0.01M Na_2S solution (Eq. (2)) using a constant energy dose (3600 pulses, 60 mJ/pulse). As mentioned previously, the addition of Na_2S increases the amount of precipitated ZnS colloid in the dark. One may observe that the total zinc and sulphur contents Zn_xS_y ($x = 0.1-0.2$, $y = 0.25-0.32$) increase, although with different slopes. This indicates a change in the deposition kinetics, favoring Zn incorporation at higher colloid concentrations. It should be noted that the higher sulphur content in the films relative to the Zn content, i.e.: $y/x \approx 2.5-1.6$ may be a conse-

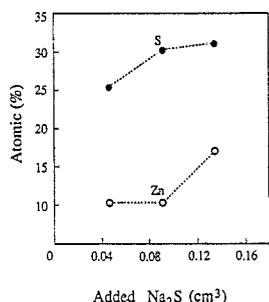


Fig. 2. XPS results (in at%) for the evolution of the total zinc and sulphur content of photodeposited films with increasing ZnS colloid concentration (added Na₂S quantity according to Eq. (2) in text). The deposited laser energy was maintained constant.

quence of two combining processes: (1) a prevailing volume photodeposition effect, by which Zn particles are precipitated in the bulk of the irradiated zone, and (2) a complex oxygen chemisorption process on the sulphur sites on the surface, leading to the formation of SO₂ like species in condensed form [14]. To elucidate the adsorption mechanisms on the surface, the chemical states of ZnS and oxygen in the films were investigated, see Figs. 3 and 4. As usual for transition metals, the XPS spectrum for Zn 2p level exhibits a doublet, with a binding energy (BE) gap of 23 eV separating the 2p_{3/2} and 2p_{1/2} components [15,16]. Figs. 3a and 3b display the Zn 2p_{3/2} and O 1s lines respectively, together with their deconvoluted spectra for a film photodeposited from a ZnS colloid sample chemically precipitated by 0.046 cm³ (0.01M) Na₂S solution. In Fig. 3a, the main peak which lies at 1022.1 eV should be associated with Zn bound in ZnS, but according to Ref. [15], sharing almost the same BE value as the elemental Zn. By comparing this result with the atomic ratios Zn/S and with the S 2p line spectrum in Fig. 4, a prevailing ZnS content of photodeposited layers may be deduced. At BE values slightly higher (1023 eV in Fig. 3a) the Zn 2p_{3/2} peak in ZnO appears. The third deconvoluted region of the Zn 2p_{3/2} line (Fig. 3a), with the peak BE at 1024.9 eV may be assigned to Zn bound in sulphate [15] which, according to Refs. [17,14], appears to be due to the interaction of chemisorbed oxygen with sulphur. According to data from the literature [14,15], the higher BE peak (532.3 eV) of O 1s level (Fig. 3b) can be assigned to the adsorption of water vapor, which most likely occurs

during the exposure of the samples to air. The two peaks in the lower energy region indicate chemisorbed oxygen species [14], which are probably oxygen bound in oxide (530.9 eV) and sulphate (530.4 eV). The analysis of the S 2p core level spectra of layers deposited from ZnS colloid with different concentrations (for various Na₂S concentrations) is shown in Fig. 4. The main peak was assigned to the S chemical state in ZnS, corresponding to a binding energy of 162.2 eV. The peak at 170.7 eV, which grows with increased ZnS colloid concentration is probably due to the chemisorption of oxygen, with the formation of SO₄²⁻-like species [14,15]. At even

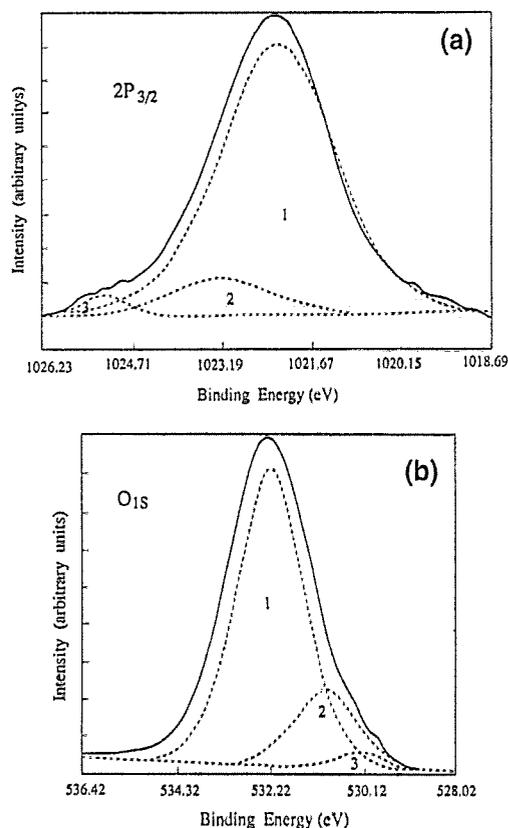


Fig. 3. (a) Zn 2p_{3/2} line and its deconvolution for a film photodeposited from ZnS colloid solution (chemically precipitated by 0.046 cm³ Na₂S). The three components are attributed to: (1) Zn bound in ZnS (1022.1 eV), with possible contribution from elemental Zn (see text); (2) Zn bound in ZnO (1023 eV); (3) Zn bound in ZnSO₄ (1024.9 eV). (b) O 1s line and its deconvolution for a film photodeposited from ZnS colloid solution (chemically precipitated by 0.046 cm³ Na₂S). The three components may be attributed to: (1) water adsorption (532.3 eV); (2) O bound in oxide (530.9 eV); (3) O bound in sulphate (530.4 eV).

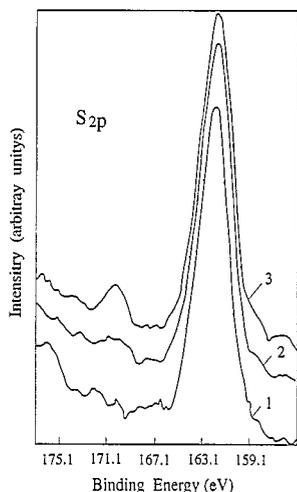


Fig. 4. XPS spectra for the S2p line. The films were obtained from ZnS colloid solutions with increasing concentrations ((1) 0.046 cm³ Na₂S; (2) 0.10 cm³ Na₂S; (3) 0.14 cm³ Na₂S). Besides the main peak (162.2 eV) attributed to ZnS, oxidizing species appear: 170.7 eV for SO₄²⁻-like species and 177 eV for SO₂ condensed species.

higher BE energies, a third peak at ~177 eV appears, which according to Ref. [14] may be attributed to the superficial formation of SO₂ condensed species by the binding of chemisorbed oxygen with S sites. From Fig. 4, this species have a higher occurrence at low ZnS colloid concentrations. This finding is in agreement with the results of the composition found from Fig. 2 indicating that the increased Zn content in the layers with increased ZnS colloid concentration is accompanied by a reduction of the rate of incorporation of sulphur into the films.

By comparing the results obtained by XPS techniques, it is likely that with increased colloid concentration, elemental Zn is also incorporated in the photodeposited layers, due to a shift of the appropriate redox potential of the photosensitized ZnS sol system.

3. Discussion and conclusions

In previous works [3–5] the photodeposition mechanisms of a-Se and metallic Cd thin films from aqueous colloid solutions were described. In all these systems the colloid particles are the light absorbing

centers creating electrons and holes which can initiate redox or oxidation processes on the surfaces. In the photoexcited suspension of CdS particles, Cd⁺ ions are adsorbed on the semiconductor surfaces [5]. ZnS is an n-type semiconductor, which can be photoactivated by photon energy in excess of its band gap energy, i.e. 2.5 eV for crystalline ZnS [20]. Hence, in our system the ZnS colloid particles should be the adsorbing centers of the UV radiation. Indeed a 55% peak optical absorption was measured at 248 nm for our ZnS colloid solution. Then the excited electrons in the conduction band may be transferred to the adsorbed ions [18] subsequently reduced to Zn⁽⁰⁾ atoms [5]. Indeed, in several works it was observed that photogenerated holes react with semiconductor surfaces, leading to surface dissolution (corrosion), through the oxidation of S²⁻ thus decreasing S⁻ radicals (which, together with conduction-band electrons are the two main reducing species) [18,20].

Acknowledgements

The authors wish to express their gratitude to Dr. C. Grigoriu for his helpful assistance with the excimer laser irradiation experiments. Also we wish to thank Dr. I. Voicu and Dr. I. Morjan for their useful advice and help with the chemical procedures involved in the experiments.

References

- [1] A. Peled, Guest Ed., Photodeposition and Related Photoassisted Thin Film Processes, *Thin Solid Films* 218 (1992).
- [2] Y. Murata, Ed., Photo-Excited Processes and Applications, *Appl. Surf. Sci.* 79/80 (1994).
- [3] M. Perakh and A. Peled, *Bull. Israeli Phys. Soc.* 22 (1976) 87.
- [4] A. Peled and Y. Dror, *Opt. Eng.* 27 (1988) 482.
- [5] V. Weiss, A.A. Friesem and A. Peled, *Thin Solid Films* 218 (1992) 193.
- [6] L. Nanai, L. Hevesi, F.V. Bunkin, B.S. Lukyanchuk, M.R. Brook, G.A. Shafeev, D.A. Jelski, Z.C. Wu and T.F. George, *Appl. Phys. Lett.* 54 (1989) 736.
- [7] M.R. Brook, K.I. Grandberg and G.A. Shafeev, *Appl. Phys. A* 52 (1991) 78.
- [8] R.R. Krchnavek, H.H. Gilgen, J.C. Chen, P.S. Shaw, T.J. Licata and R.M. Osgood, *J. Vac. Sci. Technol. B* 5 (1987) 20.

- [9] W.E. Johnson and L.H. Schie, *Appl. Phys. Lett* 40 (1982) 649.
- [10] A. Yashikawa, T. Okamoto and T. Fujimoto, *J. Cryst. Growth* 107 (1991) 653.
- [11] T. Ohno and T. Taguchi, *J. Cryst. Growth* 107 (1991) 649.
- [12] S. Fujita, S. Maruo, H. Ishio, P.A. Murawala and S. Fujita, *J. Cryst. Growth* 107 (1991) 644.
- [13] A. Peled, *Phil. Mag. B* 54 (1986) 171.
- [14] D.P. Amalnerkar, S. Badrinarayanah, S.M. Date and A.P.B. Sinha, *Appl. Phys. Lett.* 8 (1982) 270.
- [15] D. Briggs and M.P. Seah, Eds., *Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy* (Wiley, New York, 1990).
- [16] A. Lebugle, U. Axelsson, R. Nyholm and N. Martensson, *Phys. Scr.* 23 (1981) 825.
- [17] M. Lichtensteiger, C. Webb and J. Lagovski, *Surf. Sci.* 97 (1980) L375.
- [18] F.D. Saeva and G.R. Olin, *J. Chem. Soc. Chem. Commun.* (1980) 401.
- [19] A. Mills and G. Williams, *J. Chem. Soc. Faraday Trans. I*, 85 (1989) 503.
- [20] A. Davydov, *Théorie du Solide* (MIR, Moscow, 1980).