CHEMISTRY LETTERS, pp. 339-342, 1994.

Novel Electrochemical Synthesis of CdS Films from Supersaturated Solutions

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A novel method, combining chemical and electrochemical processes and involving a principle of supersaturation of the solutions, has been offered for the deposition of CdS films. A wider choice of sulphur sources and versatility in film formation are the attractive features of this method.

Historically, CdS remains one of the most immensely studied II-VI semiconductors in view of its use in photoconductive as well as photovoltaic devices. Various methods are available for producing CdS in different forms. Even a cursory glance at the literature on CdS indicates that methods for producing single crystals,[1] sintered layers/pellets,[2-4] thin films (by vacuum evaporation,[5,6] sputtering,[7] spray pyrolysis,[8] *etc.*) and thick films[9] of CdS were popular in the past while the methods for producing thin films of CdS based on the chemical[10,11] and electrochemical processes[12-19] are still gaining a lot of popularity. This is particularly because of certain inherent advantages of such methods as described by many authors.[10-13,17-19]

To further enrich the existing knowlegde on chemically and electrochemically deposited CdS films, we offer herewith a novel method which combines both the chemical and electrochemical processes for the deposition of CdS films and is based on the principle of supersaturation of the solutions. It should be noted that the method described in this letter has a strong precedent of the earlier work established by one of our authors[20] in case of compounds with low solubility such as oxalates and tripolyphosphates of silver and calcium.

In our method, electrochemical formation of CdS films was accomplished potentiostatically by using three-electrode configuration comprising an ITO-coated glass as a working electrode (substrate), a platinum foil as a counter electrode and SCE as a reference electrode. The electrochemical bath consisted of aqueous solution of hydrated salts of cadmium chloride/acetate/perchlorate acting as a cadmium source and thioacetamide (TAA)/thiosemicarbazide(TSC)/thiourea acting as an indirect sulphur source (*i.e. via* H_2S formation upon hydrolysis). All the chemicals were analytical reagent grade. The substrates were cleaned ultrasonically using acetone and isopropanol prior to actual deposition. The details of the preparation conditions and the status of CdS film formation are outlined in Table 1.

Figure 1 shows typical X-ray diffractograms for as-deposited CdS films. Both the patterns reveal occurrence of only hexagonal phase with considerable <002> preferred orientation *i.e.*, strong basal plane (0001) orientation parallel to the substrate. We also noticed that the extent of <002> preferred orientation primarily depends upon the deposition time, bath constituents and bath temperature. Figure 2 presents typical X-ray photoelectron spectrum of an as-deposited CdS film. A careful examination of XPS wide scan (0-1000 eV) suggests the formation of only CdS with the appearance of usual surface oxygen, carbon and nitrogen in the

Table 1. Preparation Conditions and Status of CdS Film Formation

Run	Bath Comp. & [pH]	Bath Temp /° C	Deposition Pot. /V vs. SCE	Deposition Time/min	Observations/Remarks
1	0.05M $CdCl_2$ +0.10M TAA, [4.6]	70	-0.50	60	No visible CdS film formation
2	-do-	70	-0.65	120-150	Formation of very thin, smooth, well-adherent and pale yellow colored CdS film
3	-do-	70	-0.65	300	Formation of thin and well-adherent CdS film
4	-do-	70	-0.70	150	Formation of less uniform, deep yellow CdS film with visible marks of gas bubbling
5	-do-	70	-0.70	225	Formation of non-uniform, patchy CdS film
6	-do-	70	-0.8 ~ -1.0	150	Deposition of Cd metal mainly
7	-do-	70	< -1.0	150	Leads to reduction of ITO
8	0.05M $CdCl_2$ +0.10M TAA + HCl, [1.85]	70	-0.65	150	Formation of relatively thick, cloudy, well-adherent, yellow colored CdS film
9	0.05M $CdCl_2$ +0.10M TAA +HCl, [1.4]	50-60	-0.65	150	Formation of relatively thick, cloudy, well-adherent, yellow colored CdS film
10	-do-	70	-0.65	150	Formation of relatively thick, less uniform, well-adherent and orange colored CdS thin film
11	0.05M $Cd(Ac)_2$ +0.10M TAA + CH_3COOH, [3.8]	50-65	-0.65	120	Formation of highly transparent CdS thin film
12	0.05M $Cd(ClO_4)_2$ +0.10M TAA, [3.3]	70	-0.65	150	Formation of very smooth, uniform, well-adherent, pale yellow colored thin CdS film
13	0.05M $CdCl_2$ +0.05M-0.06M TSC, [4.5]	75-85	-0.65	150-300	Formation of highly transparent CdS film
14	0.05M $CdCl_2$ +0.10M thiourea, [4.6]	80	-0.64	300	Formation of very thin, pale yellow colored CdS film

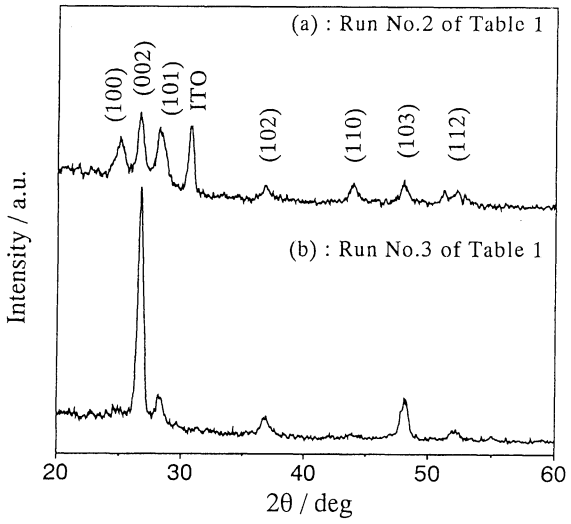

Fig. 1. X-ray diffractograms of as-deposited CdS films recorded with CuKα radiation.

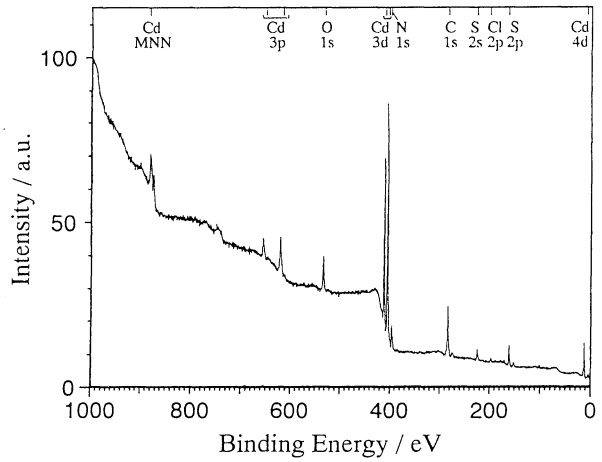

Fig. 2. X-ray photoelectron spectrum of an as-deposited CdS film recorded with MgKα radiation.

spectrum as a generalized case. For a specific case (indicated in Fig.2) dealing with bath containing $CdCl_2$, the resultant CdS film also indicates the appearance of a peak due to Cl(2p). This peak – in the first instance – can be ascribable to $CdCl_2$ entrapped/occluded in CdS film. However, it is perplexing to observe that this particular XPS peak does not disappear even after the as-deposited film has been subjected to rigorous ultrasonic washing with distilled water to remove $CdCl_2$ by solubilizing. Leaving aside such consequential findings, both XRD and XPS data confirm the formation of CdS films in the present case.

As illustrated in Table 1, this method offers a wider choice of sulphur sources (*i.e.*, TAA, TSC, thiourea, *etc.*) in contrast to conventional aqueous electrosynthetic methods which perhaps rely upon thiosulphate as the only choice of sulphur source.[13,15-19] Furthermore, it allows formation of different types of CdS films ranging from highly transparent, very thin to translucent, thick films. This versatility in film formation enables to select the right quality CdS films for the specific end applications. Quite interestingly, we have also observed an appreciable blue shift in photoelectrochemical spectral response for some of CdS films *viz.* corresponding to Run 2 and 13, though most of the samples yield normally reported value ~2.4 eV for the bandgap (Fig.3). Although we are collating more data to investigate the origin of this blue shift, apparently it might be attributable to size quantization effect which may occur in view of the particulate nature of our films. [21]

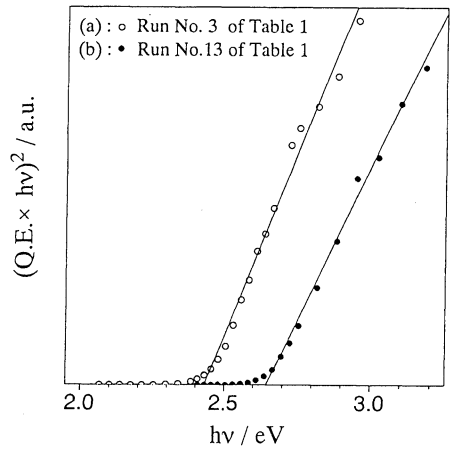

Fig. 3. Direct bandgap determination for as-deposited CdS films.

The deposition of CdS films by this new method can be presumed to proceed through following steps:

(i) Cathodic reactions (hydrogen evolution/oxygen reduction) occuring at the working electrode can lead to an increase in pH of the solution in the micro-vicinity of the working electrode.

(ii) As a consequence of step (i), the solubility of CdS can be expected to decrease only in the micro-vicinity of the working electrode. Such a situation – when confined to a condition of

supersaturation[20,22] – can result in the chemical precipitation of excess CdS (*i.e.* with respect to difference in solubility) in the form of thin film on the working electrode.

However, these steps are only speculative in nature and more investigations to understand the intricacies of basic mechanism are in progress. We discard the possibility of electrophoretic deposition taking place in this case, since the applied voltage is not sufficient for its realization.

Lastly, it might be noted that our work opens up the possibility of synthesizing (bulk as well as quantum size) variety of functional semiconductors possessing low solubility in solutions.

This work was supported in part by Grant-in-Aid for Scientific research from the Ministry of Education (No.04650727) and Iketani Science and Technology Foundation. One of our authors (D.P.A) is grateful to AIEJ for generous financial support.

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21) As evidenced by the estimates of particle size ~10-20nm(by TEM analysis) and crystallite size ~15nm (derived from Scherrer's equation using XRD data)-unpublished results.
22) Supersaturation is evident from the immediate appearance of CdS turbidity upon mixing the respective source solutions. It ensures continuous supply of S^{2-} species – a prerequisite for CdS film formation in the present case.

(Received November 9, 1993)