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Preparation of ZnS thin films from solution mist by laser irradiation

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A new type of laser chemical vapour deposition process, in which the reactants are incorporated in the mist of the solvent, is proposed. It is applicable to prepare high-quality thin films from reactants having a low vapour pressure. By using a continuous wave CO_2 laser, ZnS thin films, consisting of *c*-axis oriented ultrafine microcrystallites, have been prepared.

1. Introduction

Thin film electroluminescent (EL) display is one of the most promising technologies for emissive displays in the near future [1]. Metal sulphides such as ZnS have been used as a material for EL displays. The preparation of metal sulphide films involves some difficulties compared with that of metal oxide films. The techniques of thermal vapour evaporation and spattering exhibit many problems, such as poor stoichiometry control and high macroscopic defect densities. The application of chemical vapour deposition (CVD) to the fabrication of thin-film devices seems to be promising in combatting these problems [1]. In the CVD of ZnS thin films, metal organic chemical vapour deposition (MOCVD) using dialkyl zinc and H_2S was reported in the fabrication of EL devices [2, 3]. One of the problems in this process is the pre-reaction between dialkyl zinc and H_2S. Less reactive zinc chelates, such as zinc dialkyldithiocarbamate, were used for the deposition of ZnS on vapour phase pyrolysis [1]. Although applications of this process to the EL films have been suggested, a low pressure or a high temperature is indispensable in order to vapourize the chelates. Spray pyrolysis of the chelate solution at normal pressure exhibits difficulty in controlling the deposition conditions and hardly provides dense ZnS thin films.

In the present study, a new type of CVD process is proposed, in which the reactants are incorporated in the mist of the solvent and the vapourization was performed by intense laser irradiation under atmospheric pressure. The present method, named the laser-assisted mist CVD (LMCVD), is applicable to a wide range of substances. Because the total amount of reactants is confined to the mist, the product formed by the laser irradiation is expected to be an ultrafine particle of a uniform size. The thin film formed on the substrate by the deposition of such particles will thus probably be of a high quality. Because reactants usually absorb ultraviolet light, an excimer laser may be desirable for effective vapourization. However, a continuous wave CO_2 laser was used in the present experiment, because when practical application is considered, the cost of photons is expensive for excimer lasers compared with that for CO_2 lasers [4].

2. Experimental procedure

A schematic diagram of the LMCVD apparatus is shown in Fig. 1. The apparatus consists of three parts; a mist generator, a reaction chamber, and a laser system. The mist generator (nebulizer) is made of Pyrex glass tube, 40 mm diameter and 200 mm long. A capillary nozzle is positioned at the bottom centre of the tube and the glass tube of 10 mm diameter is connected at the top for guiding the mist into the reaction chamber. The connecting tube is as long as 300 mm to select the small mist droplets which are free from the adsorption on the tube wall. The size of the mist droplets observed with an optical microscope was about 20 μm. The meniscus of the reactant solution was set to a constant level by supplying it at the rate of about 10 $dm^3 h^{-1}$. In order to control the flow rate of the mist, a nitrogen inlet was positioned beside the capillary nozzle.

The chamber consists of an open-ended cross-shaped glass tube of 30 mm diameter. The both sides of the cross were made of larger glass tube (40 mm diameter, and 200 mm long), where gas inlets are used to form nitrogen curtains. The substrate was a quartz plate or a silicate glass plate of about 10 mm × 20 mm in size, and it was mounted on a ceramic block which contained a Kanthal wire for heating. The temperature at the surface of the sample was kept constant within ± 5 °C by a controller (Keyence TF1-10) connected to a CA thermocouple. The distance between the end of the mist guide and the surface of the substrate was varied from 10–50 mm. In most experiments the mist-drift distance was fixed to be 40 mm.

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Among the common solvents selected was *iso*-propanol which absorbs the laser beam at a wavelength of 10.6 μm. Zinc acetate ($Zn(CH_3COO)_2$) and thiourea ($SC(NH_2)_2$) were used as reactants. In order to improve the solubility, 20 vol % water was added to the solvent. The concentrations of zinc salt and thiourea were typically 0.02 and 0.04 M (M = mol dm^{-3}), respectively. Because thiourea forms a 1:2 complex with metal ions [5], zinc and thiourea presumably exist as a chelate.

The laser system used was an NAL-250D CO_2 laser (Japan Science Engineering Co.). An incident beam of about 10 mm diameter passed close above the substrate, but does not irradiate it directly. The mist flowing from the guide-end is irradiated by the laser beam, and the resultant vapour or fine particles are deposited on the substrate. The laser power, ranging from 150–200 W measured at the end of the chamber, was reduced to one-third when the mist was introduced into the chamber.

The thin films prepared were characterized by an electron microscope (SEM/EPMA, Jeol JXA-733), an X-ray diffractometer (XRD, Rigaku Denki RAD III B), a thickness gauge (Safcon 550A), a UV–vis spectrophotometer (Hitachi U-3210), and a fluorescence photometer (Shimazu RF-5000).

3. Results and discussion

Fig. 2a and b shows scanning electron micrographs of the surface of thin films prepared at different distances between the mist guide-end and the substrate. Fine micrograins are observed as in Fig. 2b, while when the distance was shorter, larger crystallites were obtained, as in Fig. 2a. When the distance was 50 mm, the finest surface was obtained but the deposition rate decreased. Thus, in the following experiments, the drift distance was fixed to be 40 mm.

Fig. 3 shows time profiles of the thickness of the film deposited on a glass substrate at 400 and 500 °C. In Fig. 4, the deposition rate is plotted as a function of substrate temperature. The deposition rate is not proportional to the concentration of zinc ions, which may be explained by the laser irradiation not being sufficient to decompose the reactants.

When the laser power was less than 130 W, ZnS thin films were not prepared in this temperature range. Thus the film formation by pyrolysis of the mist on the surface of the heated substrate did not take place under these experimental conditions. This observation can be explained by the mist being so small as to drift away from the substrate without undergoing thermal reaction.

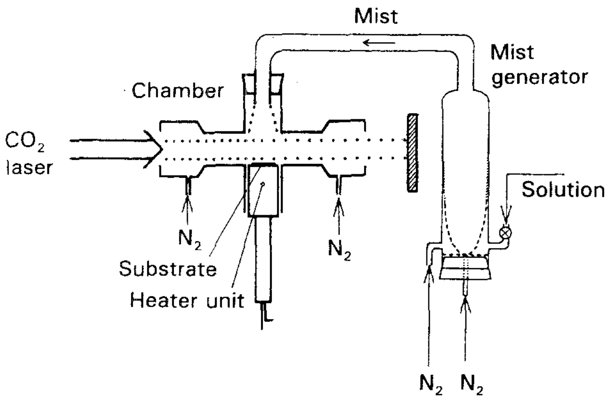

Figure 1 Schematic diagram of the apparatus for laser-assisted mist chemical vapour deposition (LMCVD).

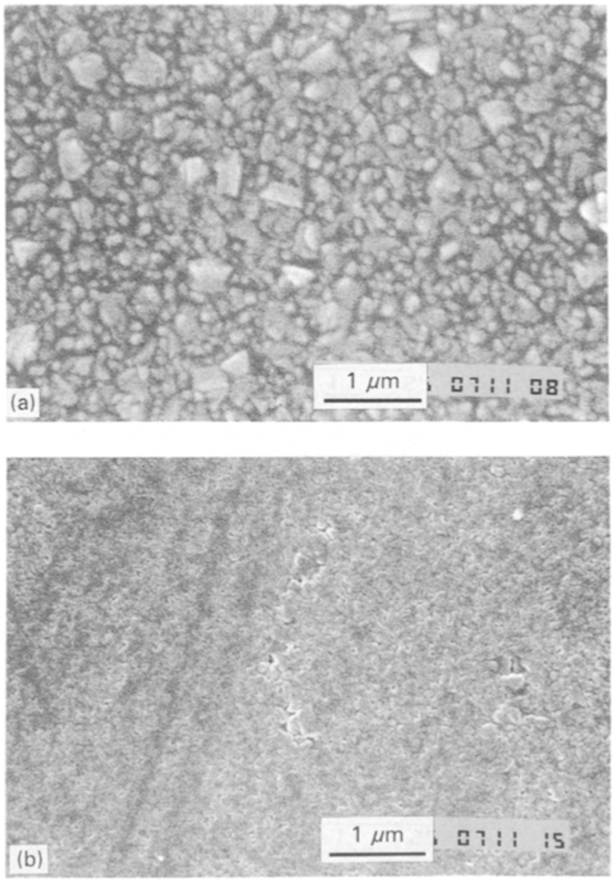

Figure 2 Scanning electron micrographs of ZnS thin film deposited for 20 min on silicate glass at 450 °C. The distance between the end of the mist-guide and the substrate was (a) 20 mm and (b) 40 mm.

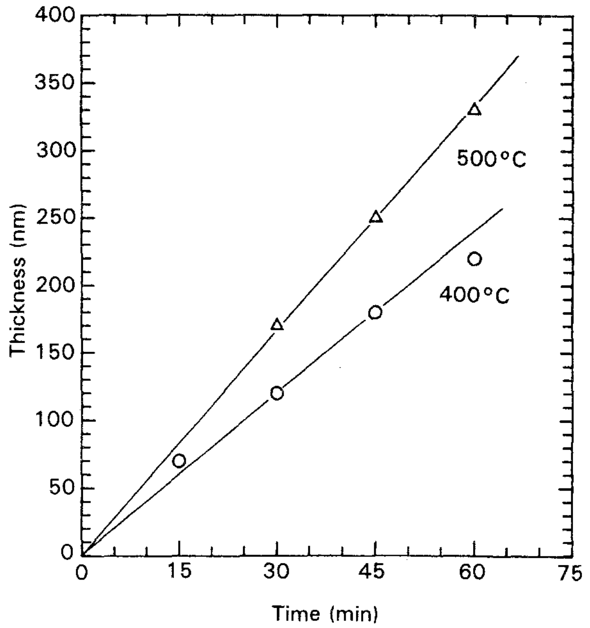

Figure 3 The thickness of ZnS film as a function of time for the deposition at the substrate temperatures of 400 and 500 °C.

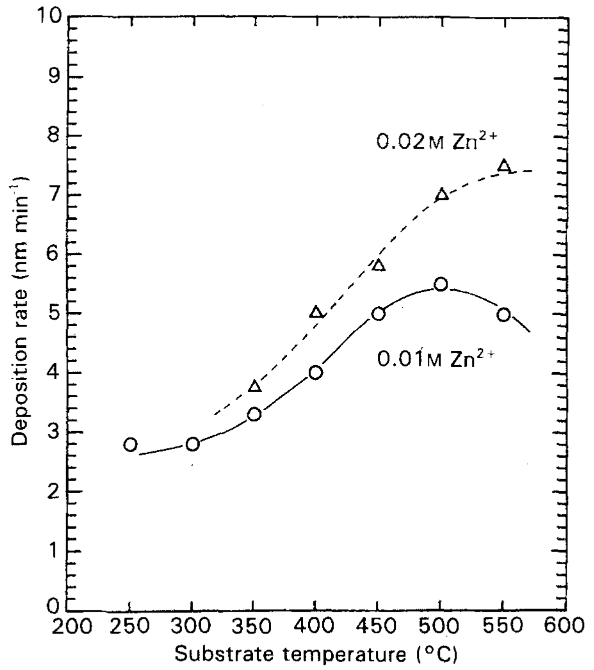

Figure 4 A plot of the deposition rate as a function of substrate temperature for two different concentrations of the reactant solution.

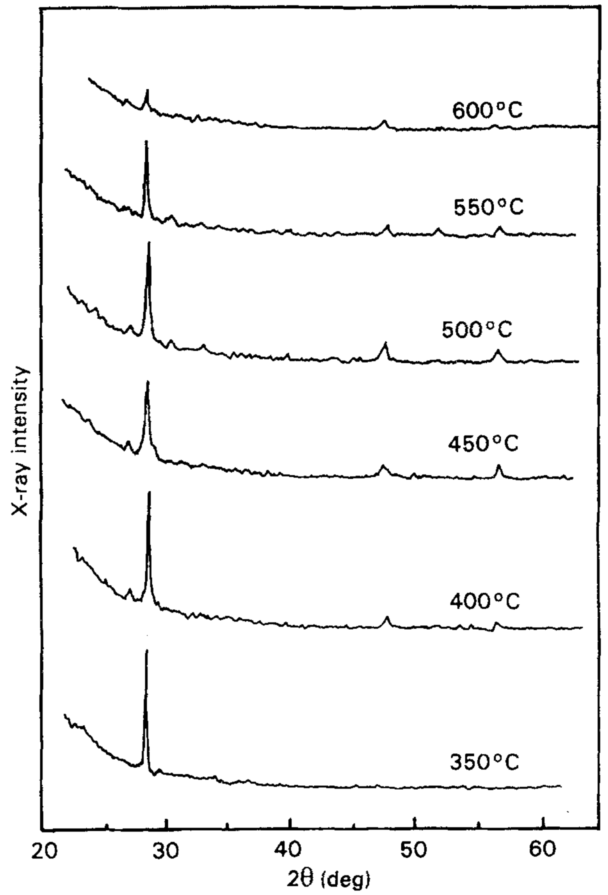

Figure 5 X-ray diffraction patterns of the ZnS thin film deposited on silicate glass for 60 min at different substrate temperatures.

Fig. 5 shows XRD patterns of thin films deposited at various temperatures. Peaks observed at 28° are attributed to the (0 0 2) plane of wurtzite ZnS. Because the intensity ratio to other peaks is large compared with the reported value for ZnS powder, it is probable that the crystallite grows in the direction of the *c*-axis.

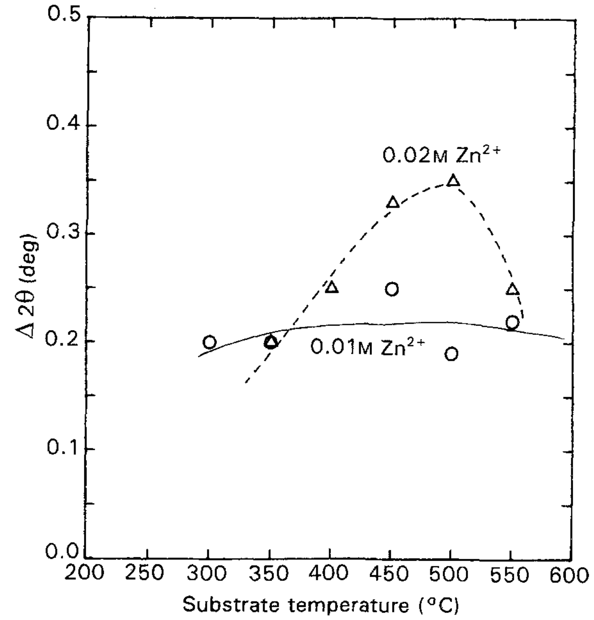

Figure 6 Width (Δ 2θ) in full-width half-maximum of the (0 0 2) peak in the XRD pattern for ZnS thin films prepared at different substrate temperatures and at different concentrations of the reactant solution.

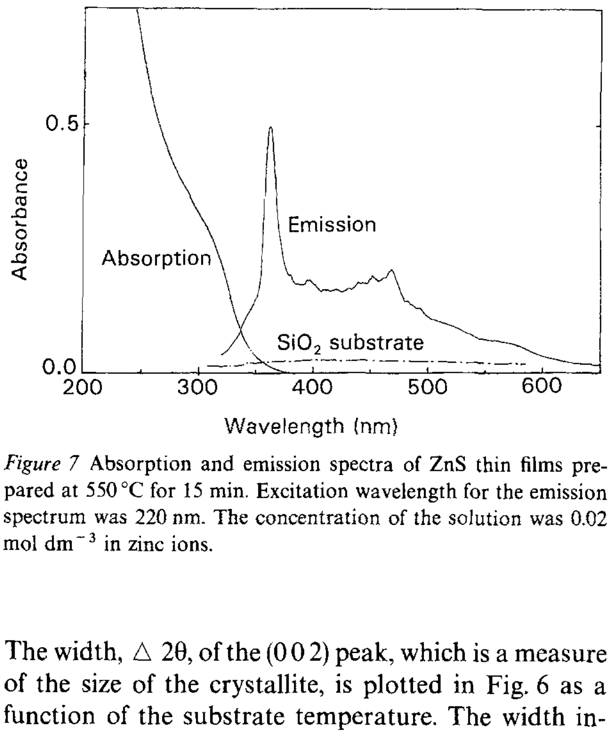

Figure 7 Absorption and emission spectra of ZnS thin films prepared at 550 °C for 15 min. Excitation wavelength for the emission spectrum was 220 nm. The concentration of the solution was 0.02 mol dm^{-3} in zinc ions.

The width, Δ 2θ, of the (0 0 2) peak, which is a measure of the size of the crystallite, is plotted in Fig. 6 as a function of the substrate temperature. The width increases with substrate temperature up to 500 °C for 0.02 M zinc ions. Comparing with Fig. 4, it is clear that the increase in the deposition rate induces the decrease in the crystalline size. This observation indicates that the deposition of the ultrafine particles on the film surface occurs so fast that it is not followed by growth to a large crystallite at the film surface. The decrease in Δ2θ at the higher temperatures suggests that larger crystallites are formed. The deposited ZnS microcrystallites combine with each other in the film bulk as well as at the surface at the higher temperature.

Fig. 7 shows optical absorption and photoluminescence spectra of the ZnS thin film deposited on a quartz plate. The bandgap energy calculated from the absorption threshold is 3.6 eV, which is comparable to that of bulk ZnS. The peak at 360 nm in the emission spectra is attributed to interband emission, indicating a negligible amount of subband levels which are caused by chemical impurities or physical defects.

In order to apply this thin film to a luminescent device, other metal ions, such as Mn^{2+} should be doped in ZnS microcrystallite. In the experiment using mists of the reactant solution which contained $MnCl_2$ or $Mn(CH_3COO)_2$, incorporation of Mn^{2+} into the ZnS film was not detected by EPMA analysis. If the irradiation was performed with a laser of higher energy density, such as an excimer laser, the metal ions might be incorporated into the microcrystallites.

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