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Hydrogen Radical Assisted CVD of ZnSe

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Hydrogen radicals are employed in the CVD growth of ZnSe. They react with starting gases to form long-lifetime precursors for deposition. The major advantages of HR-CVD over the existing methods include; 1) low temperature growth, 2) plasma free substrate, 3) selective precursor formation, 4) substrate cleaning effect, 5) rearrangement of atoms on the growing surface, 6) passivation of grain boundaries or dangling bonds. Highly (111) axis oriented ZnSe films have been prepared on glass substrates at 200°C.

1. Introduction

In recent years people have studied various methods of growing semiconductor thin films at low temperature on various substrates; e.g., glass, plastics or even on semiconductor devices in an attempt to fabricate large area electronic devices such as thin-film-transistors (TFT). These methods include MOCVD, plasma-CVD and photo-CVD. We propose, for the first time, a novel method called HR-CVD; the use of the chemical activity of hydrogen radicals in the CVD growth of ZnSe.

In HRCVD hydrogen atoms react with gaseous molecules or radicals of starting materials followed by the formation of precursor radicals. The lifetime of the radicals should be long enough to be transported to the deposition zone. The major advantages of HR-CVD over the existing methods (thrmal-, plasma-, photo-CVD) are that 1) starting materials can be decomposed at low temperature, 2) deposition can be taken place free from plasma, 3) precursors can be produced selectively by a chemical reaction. It should be noted that hydrogen radicals would be useful to improve the quality of films in various ways; e.g., in eliminating impurities by forming volatile hydrides or in passivating grain boundaries or dangling bonds. The chemical potentials associated with hydrogen radicals would be useful in the rearrangement of atoms on the growing surface. Therefore, high degree of crystallization can be attained at a low substrate temperature.

It should be noted that by employing HRCVD various materials could be prepared including silicon (amorphous[1] and crystalline), II-VI and III-V compounds and even oxides. In this paper we show the preparation of ZnSe mainly on glass substrates as a material for TFTs.

2. Experimental

The apparatus used for the preparation of ZnSe films is schematically illustrated in Fig. 1. The reaction chamber is a quartz tube, which is consisted of a plasma reaction zone and a deposition zone, eqipped with two end couplings, one for gas-inlet and the other for vacuum-pumping. A middle coupling can be inserted between the plasma reactor and the

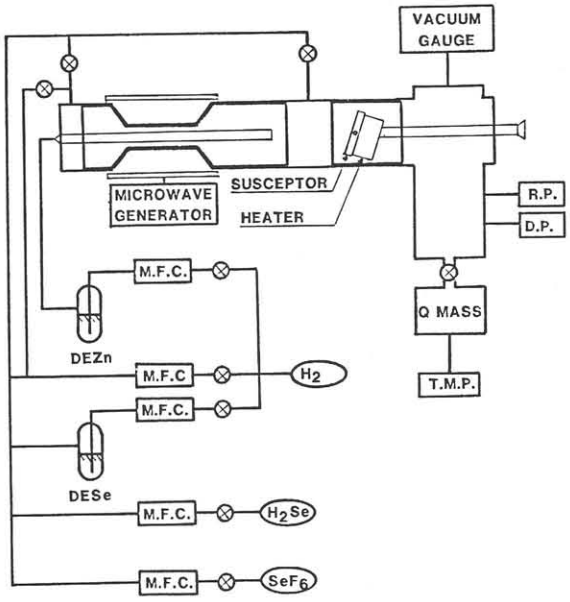

FIG. 1. Schematic diagram of apparatus used for HR-CVD of ZnSe. MFC: Mass Flow Controller, R.P.: Rotary Pump, D.P.: Difffusion Pump, T.M.P.: Turbo Molecular Pump, Q-Mass: Quadrupole Mass Spectrometer.

deposition zone, as shown in the figure, so as to introduce the reacting gas just from the vicinity of the reacting zone. The end gas-inlet coupling has two ports, one at the side and the other at the center with an o-ring sealed inner tube which made it possible to feed the gas at a desired position.

Hydrogen radicals were produced by a microwave discharge system. The major advantages of the microwave discharge are that 1) free of contamination from electrodes, 2) high density of hydrogen atoms can be produced, 3) the distribution of hydrogen plasma can be controlled by several means; e.g., magnetically, geometry of reactor tube and dilutant gases. The reactions between hydrogen atoms and diethylzinc(DEZn), H_2Se, SeF_6, and diethylselenide(DESe) have been investigated. A quadrupole mass spectrometer was employed in order to monitor the rate of decomposition of these gases against atomic hydrogen.

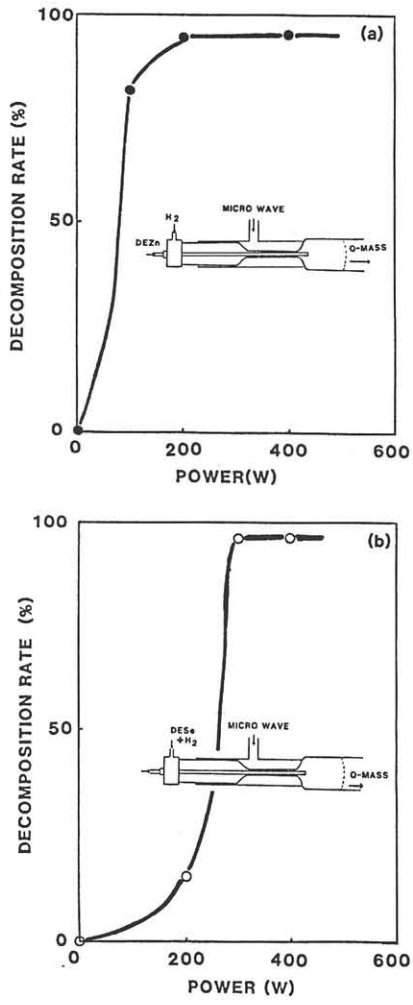

FIG. 2. The relation between the decomposition rate of source gas and microwave power for (a) DEZn and (b) DESe. The position of the gas inlet is shown in the inset.

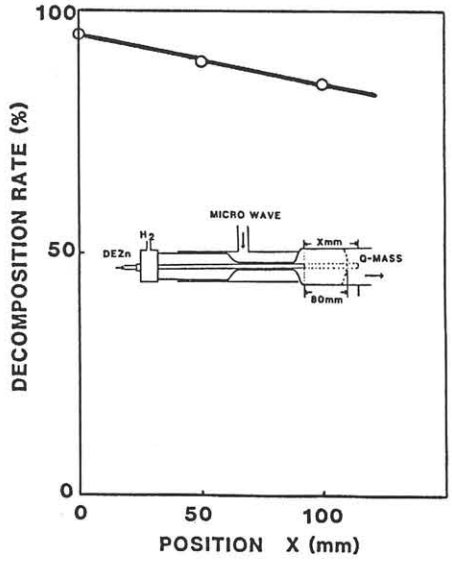

FIG. 3. The decomposition rate vs the position of the gas inlet of DEZn.

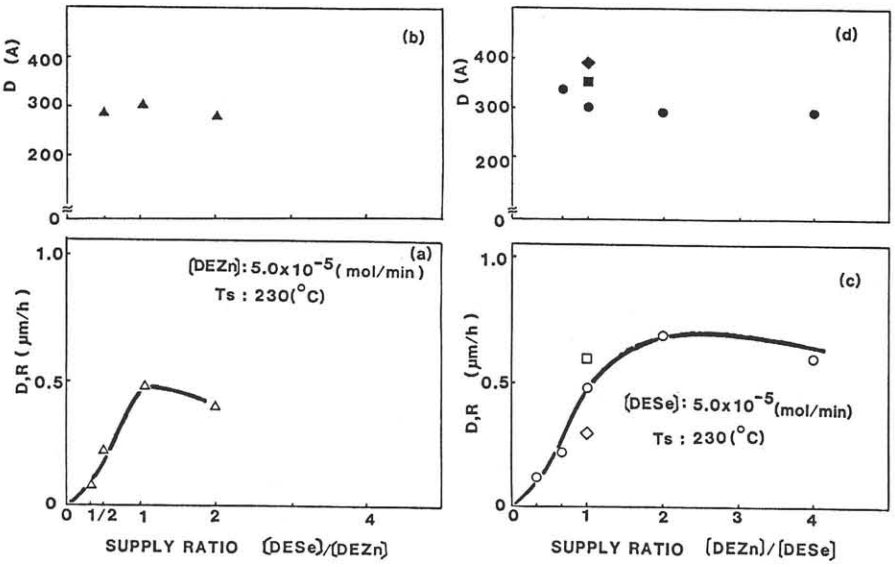

FIG. 4. (a) The deposition rates and (b) grain size of ZnSe films vs supply ratio of DESe/DEZn at a constant flow rate of DEZn. (c), (d); The same plotted as a function of supply ratio of DEZn/DESe.

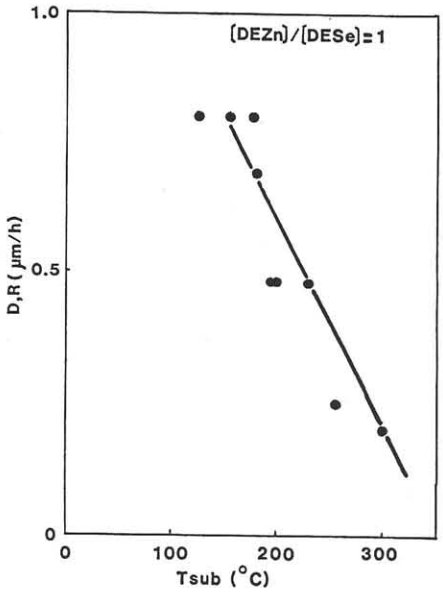

FIG. 5. The deposition rates of ZnSe films vs substrate temperature.

Properties of ZnSe films have been studied by the optical absorption, x-ray diffraction analysis, photoluminescence, electrical characteristics, RHEED, ESCA, and Auger analysis.

3. Results and discussion

It has been found that DEZn is decomposed to atomic Zn by hydrogen atoms. Figure 2(a) shows the decomposition rate of DEZn, evaluated from the reduction of the peak of mass spectra of DEZn (m/e=122), plotted as a function of microwave power. As shown in the inset, DEZn is introduced from the inner tube without any influence of the microwave, while hydrogen is fed through the outer tube giving rise a hydrogen plasma. On the other hand, DESe is not decomposed unless it is exposed to the microwave radiation. Moreover higher microwave power is required to decompose DESe rather than DEZn as shown in Fig. 2(b). The relation between the decomposition rate of DEZn and the position that DEZn gas is introduced, as defined in the inset, is shown in Fig. 3. It should be noted that the decomposition rate would not change markedly even when the gas-inlet of DEZn placed beyond the plasma region, deduced from the emission of the exited states of hydrogen radicals as indicated by a dashed curve at x=80mm in the figure. This implys that DEZn is decomposed by hydrogen radicals whose lifetime is long enough to be transported beyond the plasma region as was observed by coloring reaction of WO_3 films.

Figure 4(a) and (c) show the deposition rates of ZnSe films taken as a function of the supply ratio of DESe/DEZn at a constant flow rate of DEZn and vice versa. It should be noted that the deposition rates were determined by the flow rates of both DEZn and DESe at a low flow-rate condition.

Fig. 5 shows the correlation between the deposition rates and substrate temperature. Contrary to the case of thermal CVD, the deposition rate decreases as temperature increases. This may be due to the change of the sticking coefficient of Zn-related radicals to the glass substrate.

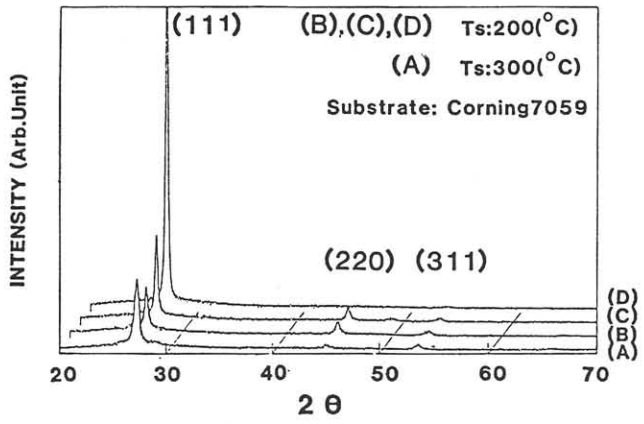

FIG. 6. X-ray diffraction curves for ZnSe films prepared at various substrate-plasma distance.

Highly (111) axis oriented ZnSe films have been deposited on glass substrates at a temperature of as low as 200C.

It has been clarified that correlations between the properties of ZnSe and the position of the substrate with respect to the plasma. Figure 6 shows x-ray diffraction curves for ZnSe films prepared by plasma CVD (A) and by HRCVD (B-D) from DEZn/DESe/H_2. In the case that substrates are located within or near the plasma, the (220) and (311) peaks are observed besides the (111) peak. Highly oriented ZnSe films are obtained when the substrate is placed apart from the plasma (curve D). The typical values of grain size evaluated from half width of the (111) peak are shown in Fig. 4(b) and (d) for various preparation conditions.

It was difficult to prepare highly oriented ZnSe films from the combination of DEZn/H_2Se because H_2Se reacts with DEZn prematurely resulting in the formation of powder of ZnSe. It was found that SeF_6 was an interesting source of Se since it was fairly stable and volatile but easily react with hydrogen radicals. Although we have not found the optimum condition for the preparation of ZnSe from DEZn/SeF_6 system, this might be a possible candidate for the CVD growth of ZnSe films.

The feasibility of the epitaxial growth of ZnSe on GaAs by employing HRCVD are being investigated.

4. Conclusions

1) Hydrogen radicals are employed in the CVD of ZnSe films. They react with starting gases to form long-lifetime precursors selectively.
2) The major advantages of HR-CVD over the existing methods (thermal-, plasma-, photo-CVD) include; a) low temperature growth, b) plasma free substrate, c) selective precursor formation, d) substrate cleaning effect, e) rearrangement of atoms on the growing surface, f) passivation of grain boundaries or dangling bonds.
3) It has been found that DEZn is decomposed by hydrogen radicals. Among the sources of Se investigated, DESe is most stable; hydrogen plasma is required to form alkyl-Se precursors. H_2Se is too reactive to control the deposition of ZnSe films. SeF_6 is an interesting source since it is stable and voltaile but highly reactive with atomic hydrogen and Zn-related radicals.
4) Highly (111) axis oriented ZnSe films have been prepared on glass substrates at 200°C by HR-CVD of DEZn/DESe/H_2 system.

References

1) S. Oda, S. Ishihara, N. Shibata, S. Takagi, H. Shirai, A. Miyauchi, and I. Shimizu: to appear in the Proceedings of the 11th International Conference on Amorphous and Liquid Semiconductors, Rome, 1985.