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Photoluminescence and Raman studies of CdS films grown by metal-organic chemical vapor deposition on Si{111} substrates

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Abstract

CdS epitaxial films grown using metal-organic chemical vapor deposition on Si{111} substrates at growth temperatures ranging from 270 to 325 °C have been characterized using photoluminescence and Raman spectroscopy. Out of all the samples the best optical behavior is obtained from that grown at the lowest temperature. Samples grown at the lowest temperature exhibited increased intensity of the bound excitonic peaks and reduced emission at the defect-related luminescence region. The Raman spectra were compatible with the film surface being normal to the *c* axis, indicating a preferred growth orientation.

1. Introduction

In recent years the interest in the growth and properties of II-VI compounds on alternative semiconducting substrates has increased because of their potential applications in monolithically integrated electronic devices. In particular, the CdS-Si combination is attractive since it possesses potential for the fabrication of integrated optical and electronic devices on the same chip. In addition, CdS is a large band gap semiconductor with a room temperature band gap of 2.42 eV and hence may also serve as a good window material for heterojunction solar cells [1-3]. Successful realization of the technological potential requires the ability to fabricate high quality material with well-defined and controlled electronic properties. In this paper we present characterization information on metal-organic chemical vapor deposition (MOCVD) grown CdS onto Si{111} substrates. We have analyzed the optical behavior using photoluminescence (PL) and Raman scattering (RS) to gain an insight into the electronic and structural behavior of the material.

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The growth of CdS has been demonstrated on several substrates by vapor phase growth methods such as CVD [4], hydrogen transport of the elements [5], hot wall epitaxy [6], MOCVD [7-10], and electron beam evaporation [11]. The substrates used were CdTe [4], InP [5], GaAs [9, 10], and silicon [7, 8, 11]. Epitaxial layers of CdS have been deposited on silicon substrates by earlier workers using electron beam evaporation [11] and MOCVD [7, 8]. In this work we describe the PL and RS results obtained from CdS films grown on Si{111} substrates. The films were grown using a horizontal low pressure MOCVD system [7]. The samples used here have been investigated earlier using X-ray diffraction and the results have been reported by Boone *et al.* in ref. 7. Cross-correlation with the structural information is made wherever warranted.

2. Experimental details

2.1. Sample growth

Thin films of CdS were grown onto Si{111} wafers using a horizontal MOCVD system. The system consisted of a modified vertical reactor. The reactant materials used were H_2S diluted in helium (0.97%) and dimethylcadmium in a stainless steel bubbler main-

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TABLE 1. Film thickness and growth temperature of the samples used in this study

Sample	Thickness (μm)	Growth temperature (°C)
a	5.0	325
b	6.4	300
c	5.7	280
d	4.4	270

Note that all these samples were characterized using X-ray diffraction in ref. 7.

tained at 0 °C. Helium was used as the principal carrier gas whereas nitrogen and hydrogen aided in purging the system and treating the substrate respectively. For more efficient use of the reactants an electronic device was used to oscillate and heat the substrate. The substrate treatment involved the hydrogen reduction of the substrate surface at an elevated temperature. It was followed by a brief interval for establishing the flow stream, consisting of H_2S diluted in helium, across the substrate surface maintained near the growth temperature. Reactant streams containing the group II and group VI species were maintained separately prior to mixing near the flow tube outlet. The deposition time for each of these samples was 1 h. First the deposited films were characterized by X-ray diffraction. More details about the MOCVD system, growth parameters and X-ray results were given elsewhere [7, 8]. The thicknesses of the films were in the range 4–6 μm and the growth temperature ranged from 270 to 325 °C; details are shown in Table 1.

2.2. Optical measurements

The optical measurements were performed using a standard PL and RS facility that made use of a 0.85 m focal length double-pass spectrometer equipped with a cooled GaAs photocathode–photomultiplier; the monochromator resolutions were 0.25 meV and 1.5 cm^{-1} respectively for PL and RS measurements. The excitation was provided by the 457.9 nm line of an argon ion laser. The RS measurements were performed in the backscattering configuration and both polarization states of the scattered radiation were detected together. All measurements were performed at a sample temperature of 8 K.

3. Results and discussion

3.1. Photoluminescence

The results of the PL measurements are presented in Fig. 1. The curves are labeled from a to d in descending order of the growth temperature. A broad feature at

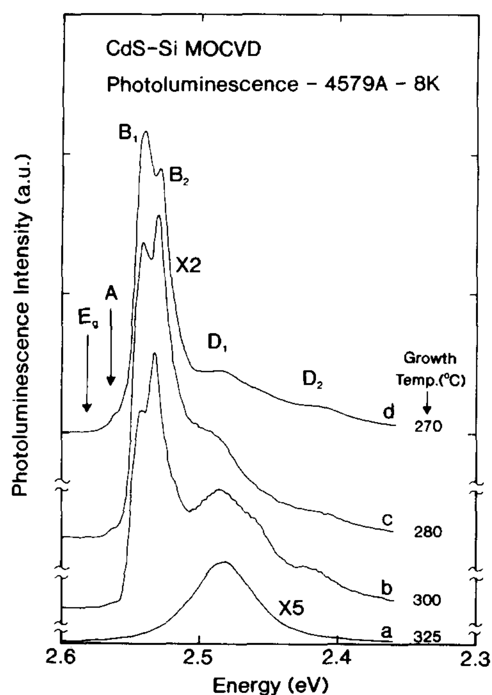

Fig. 1. PL spectra measured from the four CdS/Si samples grown at different temperatures. Sample a was grown at 325 °C, the highest temperature, and sample d at 270 °C, the lowest temperature. The band gap energy E_g is indicated for reference.

2.487 ± 0.003 eV, labeled D_1, is present in all the spectra while a qualitatively similar broad feature, D_2, is present at 2.42 ± 0.005 eV in spectra b, c and d. Two sharp and intense features are present at 2.542 ± 0.002 and 2.532 ± 0.003 eV (peaks B_2 and B_1) and a weak feature is identifiable at 2.564 ± 0.001 eV (peak A) in all but spectrum a. In comparison, the spectrum obtained from a reference sample of bulk CdS contains an intense and very sharp peak at 2.544 ± 0.0005 eV and a broader and weaker feature at 2.554 ± 0.001 eV. Weaker features are present at lower energies but are visible only when the scale is expanded by a factor of 100.

The PL spectra displayed in Fig. 1 indicate a clear trend with the growth temperature. The weakest, broadest and least interesting spectrum is obtained with sample a, grown at the highest temperature, namely 325 °C, whereas the opposite is true with that obtained from sample d, which was grown at the lowest temperature at 270 °C. The salient reference energies in photoluminescent behavior of CdS may be obtained from the literature as well as the spectra obtained from a high quality bulk sample. The highest energy feature normally observed from CdS occurs at 2.553 eV [10, 12, 13] and has been assigned to arise from the free exciton (FE) associated with the highest energy valence band extrema at the Brillouin zone center. In order of decreasing energy, the FE feature is followed by a series

of very sharp lines that arise from excitons bound to donors and acceptors (D–X and A–X), followed by broad features that originate in donor-to-acceptor pair (DAP) features and free-to-bound state transitions (A–e and D–h). The clearest indication of very high material quality is the presence of an intense FE feature with no impurity-related peaks; this implies material purity as well as good crystalline quality and the absence of defects, stray electric fields *etc.*, that can quench the FE feature. The presence of impurities will enhance the bound excitonic structures at the expense of the FE intensity. Large amounts of impurities will lead to the complete quenching of all the excitonic features leaving only the broad low energy peaks observable. The reference spectrum obtained from a good quality bulk specimen exhibits both the FE peak at 2.554 eV and bound exciton feature at 2.544 eV.

Following this line of argument, the systematic changes seen in the PL spectra from the CdS–Si(111) films suggest a distinct improvement with reducing growth temperature. Sample d, grown at 325 °C, the highest temperature, shows no evidence of any excitonic features. The broad and weak feature (D_1) at 2.487 eV most likely arises from a series of DAP transitions; the qualitatively similar broad peak seen at 2.42 eV is also expected to originate in DAP transitions. On the contrary, the sample grown at the lowest temperature, *i.e.* sample d, clearly shows the most intense high energy peak (B_1) at 2.542 eV that appears to originate in bound excitons and an associated reduction of the DAP band strength. The 2.532 eV peak (B_2) seen in samples b, c and d probably also originates from bound excitons. However, the absence of a clear FE feature in any of the samples strongly suggests that they contain a large quantity of electronic impurities and defects. The line widths of the excitonic features are probably due to broadening of the individual peaks as a result of residual strain, electric fields *etc.* as well as to the presence of closely spaced peaks merging together.

The origin of the highest energy feature (A) that appears as a shoulder at 2.564 eV is not clear. It may arise from transitions involving a shallow impurity state or from the higher energy exciton that is observed at 2.57 eV in reflection studies.

In ref. 7 it was stated that the sample grown at highest temperature (325 °C) had the best crystalline structure and those results were obtained by an inspection of the integrated area of one of the X-ray diffraction peaks. The PL results contradicts the conclusions of ref. 7. This apparent contradiction can be reconciled if one considers the nature of the two probes, namely X-rays *vs.* visible photons. The X-ray measurements penetrate through the film and well into the substrate, but the PL information is obtained mostly from the near surface region extending to a depth of 1 μm or less. Hence if one were to exclude the near-interface region that is expected to be of a very poor structural quality owing to the 7% lattice mismatch, the results of this study are probably more directly indicative of the best growth that could be achieved at a given temperature. In addition, since electronic devices will be fabricated in the region closest to the surface, the results obtained here are more directly relevant for characterization purposes.

The change in the measured energy gap from the tensile strain due to the different thermal expansion of CdS [14] and silicon [15] was estimated. Using deformation potential values reported by Langer *et al.* [16] and known values of the elastic constants [17] this change was estimated to be −8 meV (in agreement with ref. 6, the film surface was assumed to be normal to the crystal axis *c* for the calculations). Even though the PL features observed here are broad, their energy positions are incompatible with such a large energy shift. Hence, we conclude, in agreement with the results of the X-ray analysis, that the sampled volume is relatively free of strain. Similar results were obtained earlier with CdS grown on GaAs substrates [9].

The implications of the results for further optimizing the growth of CdS on Si(111) are that the large changes observed to occur in the relatively small temperature range strongly suggest that much more careful "tuning" is necessary to locate the optimum growth temperature. This may occur below the lowest temperature used here, namely 270 °C.

3.2. Raman scattering

The Raman spectra measured from the four samples used in this study are presented in Fig. 2. The spectra were recorded over the frequency range from 100 to 350 cm^{-1} that spans the one-phonon scattering region.

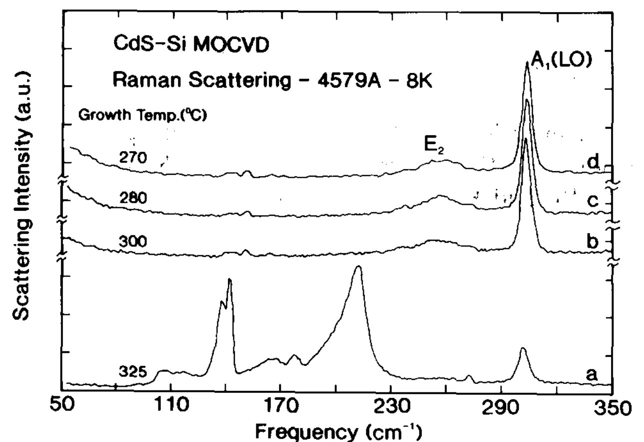

Fig. 2. Raman spectra measured from the four samples. Sample a was grown at 325 °C, the highest temperature, and sample d was grown at 270 °C, the lowest temperature.

A minimum of two distinct features are present in all the spectra. A sharp peak is observed at about 303 cm^{-1} (labeled A_1(LO)) and a weaker and broader structure can be observed at 257 cm^{-1} (labeled E_2). Low frequency features in the range from 100 to 220 cm^{-1} are present only in spectrum a.

The observed features in the Raman spectra measured from samples a–d are interpreted on the basis of earlier investigations, particularly the piezospectroscopic Raman study of Briggs and Ramdas [18]. The features observed here at 257 and 303 cm^{-1} have been studied in detail in CdS and are known to arise from lattice dynamical oscillations with the E_2 and A_1 symmetry, with the latter possessing a longitudinal polarization, hence the label A_1(LO). The presence of only these two features is only compatible with the *c* axis of the film being normal to the film surface. This observation is in agreement with the conclusions of the X-ray investigation of ref. 7, that found that the films exhibited a large degree of preferred orientation similar to that seen here.

For sample a, grown at the highest temperature, additional features are observed at 117, 142, 166, 178 and 212 cm^{-1} which cannot be related to the CdS film or the underlying silicon substrate. These vibrational bands may be indicative of foreign material incorporated either on the surface or in the film itself. While we are unable to identify the source, the RS results are compatible with those obtained using PL, *i.e.* the poorest quality film seems to be the only one with the "contamination".

The linewidths (full width at half-maximum (FWHM)) of the A_1(LO) feature of the sample are comparable and are about 5 cm^{-1}, which is significantly larger than the approximately 3 cm^{-1} FWHM observed from the crystalline sample. As pointed out earlier, the quality of the films is significantly poorer than that of the bulk reference specimen.

4. Conclusion

In conclusion, we have investigated the optical behavior of MOCVD grown epitaxial CdS on Si{111} using PL and RS. The growth temperature was varied from 270 to 325 °C and the resultant changes in the spectroscopic behavior were analyzed to gain an insight into the details of the materials growth. The results obtained in this study have been compared and contrasted with an earlier X-ray structural investigation. We find that the best materials quality is obtained for the film grown at 270 °C and the poorest is to be achieved at the highest temperature of 325 °C. In all cases, the material quality was significantly poorer than that of a bulk reference crystal. This strongly suggests that substantial improvements are necessary before MOCVD growth of CdS on Si{111} is likely to see any technological use.

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