JOURNAL OF MATERIALS SCIENCE 13 (1978) 1449–1454

Direct synthesis and structure of epitaxial cadmium sulphide layers on cadmium single crystals

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Epitaxial cadmium sulphide layers, 300 to 1500 Å in thickness, have been grown by direct synthesis on the basal face of cadmium single crystals. The reaction Cd + S → CdS was carried out in sealed glass ampoules evacuated up to 10^{-6} torr. The morphology, phase structure and epitaxy of the films were investigated by electron microscope, electron and X-ray diffraction techniques. It was found that the film lattice had a wurtzite-type (hexagonal) structure. The epitaxial layers were produced at substrate temperatures of 150 to 310° C with sulphur vapour pressures of 6×10^{-4} torr. It was found that $\{0\,0\,0\,1\}$ CdS $\parallel \{0\,0\,0\,1\}$ Cd with $\langle 1\,1\,\bar{2}\,0\rangle$ Cd.

1. Introduction

Due to its optoelectronic properties CdS is important in the production of semiconductor devices and terrestrial solar cells. This fact makes CdS one of the most investigated A(II) B(VI) compounds.

Thin CdS layers have often been obtained by vacuum evaporation [1–30], evaporation through a gas discharge [31], vapour deposition in hydrogen atmosphere [32, 33] and in a nitrogen stream [34], chemical transport reactions [35–45], reaction of the metal vapours with the nonmetal hydride gases [46], cathodic sputtering [47–50] and so on. Depending on the deposition conditions CdS layers consist of only one phase or a mixture of two phases. Usually either the wurtzite phase is obtained [3, 5–8, 20–28, 30, 32–50] or simultaneously wurtzite- and sphalerite-type [2, 4, 9, 13–17, 19–28, 42]. In some cases, under definite conditions, CdS-sphalerite type has been found [1, 10, 16, 19, 22–26, 28, 35, 42, 47–50]. CdS with a NaCl-type lattice appears rarely and only under special conditions [17]. Glass, quartz, mica, sapphire, NaCl, KCl, KBr, BaF_2, CaF_2, SrF_2, GaAs, GaP, InP, InSb, Ge, CdS, ZnS, ZnTe, MoS_2 etc. have been used to verify the epitaxial action of the substrate. Mica, glass, quartz covered in advance by Au [8, 9, 17, 18], Ag [13–16, 18], Cu [13–15, 18], Al [18], Pt [18] as well as Mo foil [10] have been used too. On the other hand Weissmantel *et al.* [51, 52] reported investigations on the sulphidation of evaporated zinc and cadmium films. To our knowledge no detailed experiments have been reported on the epitaxy and structure of CdS layers on metal single crystal substrates.

The method of direct synthesis of epitaxial ZnS layers on zinc single crystal substrates, developed by us [53, 54], is now applied to CdS. The results of an investigation on the morphology, structure and epitaxy of the CdS layers, produced by this method, are described in the present paper.

2. Experimental

Thin CdS films were synthesised on cadmium single crystal substrates with well-developed $\{0\,0\,0\,1\}$, $\{1\,0\,\bar{1}\,1\}$ and $\{1\,0\,\bar{1}\,0\}$ faces (Fig. 1) in the apparatus described in detail earlier [53, 54]. The sulphur vapour was condensed on the crystal surface and reacted there with the metal substrate for 2 to 7 h. The substances used were 99.9999% pure cadmium and spectrally pure sulphur, both purified additionally by repeated sublimation and distillation under vacuum (10^{-6} torr). The synthesis of CdS layers was performed in sealed glass ampoules, evacuated to 10^{-6} torr. The CdS films were cleaned completely of non-reacted sulphur by means of CS_2.

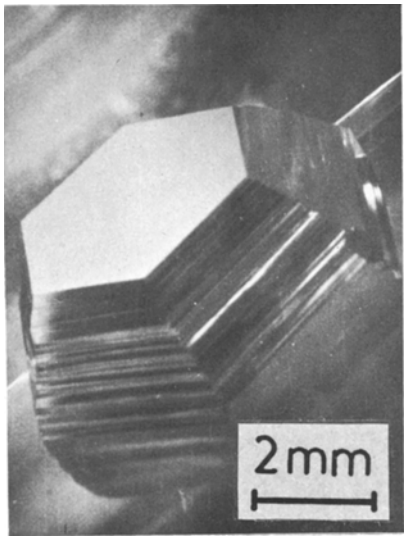


Figure 1 Cadmium single crystal used as substrate for CdS layer growth.

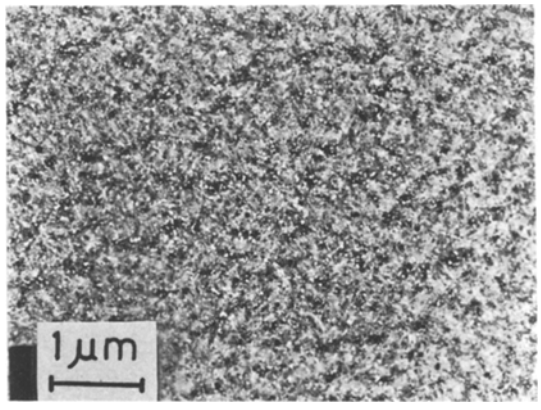


Figure 2 Transmission electron micrograph of a CdS layer, removed from the $\langle 1\,1\,\bar{2}\,0\rangle$ face of the substrate. Growth conditions: substrate temperature 300° C, sulphur vapour pressure 6×10^{-1} torr.

The thicknesses of the layers were roughly evaluated interferometrically and by their transmission characteristics with respect to electrons of differing accelerations [53, 54]. The thicknesses ranged between 300 and 1500 Å.

CdS films, together with the supporting crystals, were investigated by means of reflection electron diffraction and an X-ray texture goniometer. Then the layers were removed from the substrates by an electrochemical dissolution of the cadmium single crystals in a 1 N solution of $CdSO_4$ [55] and were studied by means of transmission electron microscopy, electron and X-ray diffraction. Some of the thinner films were stabilized by the evaporation of carbon on them.

3. Results

3.1. Morphology

During the reaction with sulphur vapour the cadmium single crystals lost their initial metallic glitter, which fact pointed to the formation of CdS layers on them. The films produced at substrate temperatures 150 to 270° C were golden, but the layers obtained at temperatures 270 to 310° C were dark coloured (especially the layers on the pyramidal and the prismatic faces).

Optical and scanning electron microscope investigations showed that the films repeated well the steps on the cadmium single crystals as well as all peculiarities of their surface structure. Transmission electron microscopy (Figs. 2 and 3) confirms this conclusion. It is seen that the films obtained on the $\{0\,0\,0\,1\}$ face exhibit a uniform structure (Fig. 2) without steps on it. The layers removed from $\{1\,0\,\bar{1}\,0\}$ and $\{1\,0\,\bar{1}\,1\}$ faces (Fig. 3) repeated the surface of the crystal including numerous steps and growth details. Like the ZnS [53, 54], the CdS layer can be used also as an electron microscopic replica of the growing cadmium single crystal, this procedure being more convenient than the preparation of a C–Pt replica under these conditions.

Whiskers and filaments grew from the CdS films on the basal face of the cadmium single crystals. At substrate temperatures between 270 and 290° C whiskers grew on the surface steps, repeated by the CdS film; at temperatures below 270° C no whiskers were observed. Some whiskers grew at angles of 60° and 120° with respect to the steps.

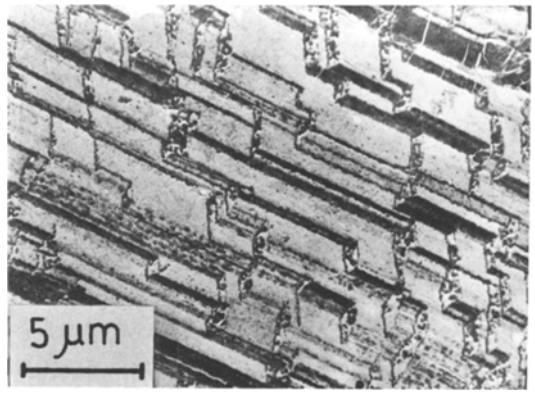


Figure 3 Transmission electron micrograph of a CdS layer, removed from pyramidal (or prismatic) regions of the substrate. Growth conditions: substrate temperature 238° C, sulphur vapour pressure 7×10^{-2} torr.

Whiskers and filaments grew also on the smooth regions of the films obtained on the basal face at the higher substrate temperatures and sulphur vapour pressures. At temperatures in the interval 290 to 310° C the majority of the smooth regions was covered by randomly grown whiskers. Other authors [51, 52, 56] also observed whiskers and filaments.

3.2. X-ray diffraction investigations

The phase structure of CdS layers was investigated by the Debye–Scherrer method, removing [55] and powdering the layers. The X-ray patterns obtained were compared with the X-ray patterns of specially prepared powder samples of CdS with hexagonal* and cubic† lattices. It was found that the CdS films were hexagonal in phase. The lattice parameters calculated here were $a = 4.13 \pm 0.01$ Å and $c = 6.70 \pm 0.01$ Å.

The orientation of the CdS layer on the basal face of the cadmium single crystal substrate was determined using an X-ray texture goniometer. Comparing the data obtained by means of the texture goniometer with the substrate orientation, it was easy to establish that $\{0\,0\,0\,1\}$ CdS ∥ $\{0\,0\,0\,1\}$ Cd and $\langle 1\,1\,\bar{2}\,0\rangle$ CdS ∥ $\langle 1\,1\,\bar{2}\,0\rangle$ Cd.

3.3. Reflection electron diffraction studies

CdS layers on the $\{0\,0\,0\,1\}$ faces of the Cd single crystals were investigated by reflection electron diffraction. The CdS layers obtained at substrate temperatures 150 to 270° C with sulphur vapour pressures 6×10^{-4} to 1×10^{-1} torr were epitaxial (Fig. 4). The films obtained in the temperature interval 270 to 310° C with sulphur vapour pressures from 1×10^{-1} to 2.5 torr showed ring electron diffraction patterns. This fact is probably due to the presence of whiskers on the layers: as seen in Fig. 5a, some of the whiskers grew non-orientated. A hexagonal structure was also found from these ring electron diffraction patterns. The values of the lattice parameters calculated for the CdS layers from the electron diffraction patterns very nearly coincide with the data obtained from the X-ray diffraction patterns.

The epitaxial layers obtained on the basal faces were examined at two different azimuthal orientations of the cadmium single crystal substrates with respect to the incident electron beam.

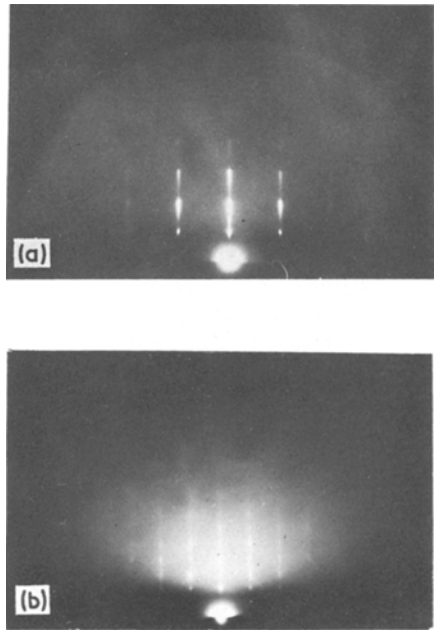


Figure 4 Reflection electron diffraction patterns of a CdS layer: (a) electron beam ⊥ $\langle 1\,1\,\bar{2}\,0\rangle$ Cd; (b) electron beam ⊥ $\langle 1\,0\,\bar{1}\,0\rangle$ Cd. Growth conditions: substrate temperature 260° C, sulphur vapour pressure 5.5×10^{-2} torr.

(a) electron beam normal to the $\langle 1\,1\,\bar{2}\,0\rangle$ direction (see Fig. 4a for the reflection electron diffraction pattern);

(b) electron beam normal to the $\langle 1\,0\,\bar{1}\,0\rangle$ direction (see Fig. 4b for the reflection electron diffraction pattern).

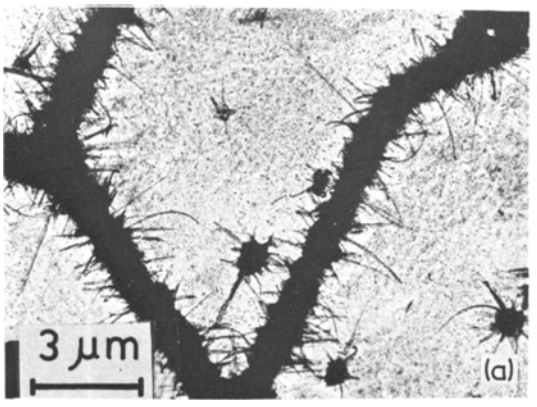
These results confirmed the epitaxial CdS/Cd orientation relationship reported above.

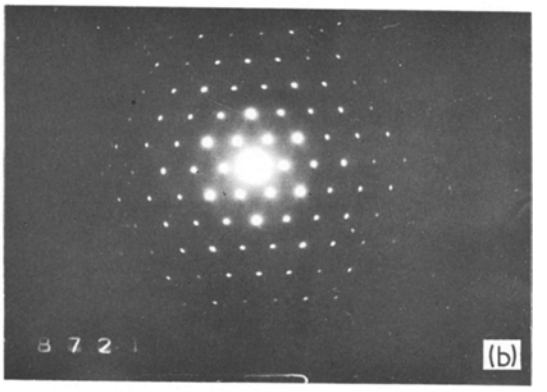
3.4. Transmission electron diffraction investigations

It was found that the layers obtained on the basal faces of Cd single crystals at substrate temperatures 150 to 310° C with sulphur vapour pressures of 6×10^{-4} to 2.5 torr were epitaxial (Fig. 5b), but the layers on the pyramidal and prismatic faces of the substrate were only partially oriented (Fig. 5c) under the same growth conditions. The latter electron diffraction pattern confirms that the CdS layers are hexagonal phase.

Comparison of the transmission electron diffraction patterns with the electron micrographs of the CdS replicas (the latter determining the substrate crystallographic orientation) made it possible

*Hexagonal CdS was obtained by heating a commercial product, which is a mixture of sphalerite and wurtzite phases, at 900° C in a quartz ampoule under a vacuum of 10^{-6} torr for 3 h, the structure being fixed by hardening.
†Cubic CdS (sphalerite-type) was obtained by hydrogen sulphide precipitation from $CdSO_4$ solution [57].





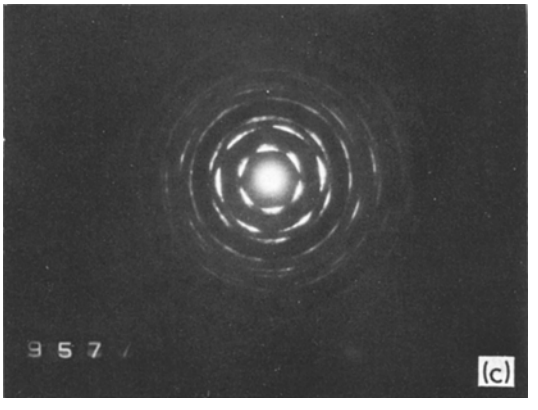


Figure 5 (a) Electron micrograph of a CdS layer with whiskers. Growth conditions: substrate temperature 290° C with a sulphur vapour pressure 9×10^{-1} torr. (b) Transmission electron diffraction pattern from the same layer (the smooth region between the steps is imaged). (c) Transmission electron diffraction pattern from a CdS layer grown at substrate temperature 238° C with a sulphur vapour pressure 7×10^{-2} torr. The layer is removed from a pyramidal region of the substrate.

to establish again the azimuthal epitaxy of the CdS layers. In this way we found that the steps on the basal faces of the Cd single crystals oriented along $\langle 1\,1\,\bar{2}\,0\rangle$ are parallel to the $\langle 1\,1\,\bar{2}\,0\rangle$ crystallographic direction in the CdS layers, as seen in Figs. 5a and b.

4. Discussion

Epitaxial CdS layers were obtained by the method of direct synthesis at comparatively low temperatures. The phase structure investigations performed by X-ray and electron diffraction techniques have shown that the CdS films are hexagonal phase (wurtzite-type). This result corresponds with the results of other authors [5–7, 11, 13–15, 18, 22–26] using different methods and substrates at the same temperatures. The epitaxial orientation relation, established by three independent methods, is that the $\{0\,0\,0\,1\}$ plane of the CdS layers is oriented parallel to the $\{0\,0\,0\,1\}$ face of the Cd single crystals, $\langle 1\,1\,\bar{2}\,0\rangle$ CdS being also parallel to $\langle 1\,1\,\bar{2}\,0\rangle$ Cd. A lattice parameter discrepancy of about 39% ($a_{CdS} = 4.13$ Å, $a_{Cd} = 2.97$ Å) can be calculated here. Nevertheless the CdS layers on $\{0\,0\,0\,1\}$ face are epitaxial. The films grown on the other faces of the substrate ($\{1\,0\,\bar{1}\,1\}$ and $\{1\,0\,\bar{1}\,0\}$) with the technique used here were only partly oriented.

In our experiments CdS layers were obtained on growing cadmium crystals in vacuum sealed glass ampoules, without any pretreatment of the substrate. We should mention that even under vacuum 10^{-6} torr no oxide is present on the crystal surface because in the closed glass ampoule the oxygen is gettered by the Cd itself (CdO hardly evaporates at these temperatures). On the other hand, oxidation, and generally contamination, is unavoidable by any pretreatment of the metal substrate. Therefore we can expect that the metal/semiconductor contact in the case under consideration may be relatively clean. Anyway this aspect of the work requires further investigation.

We suggest that the reaction between sulphur and cadmium proceeds by the diffusion of the latter substance in the formed CdS layer.

(1) The diffusion coefficient for cadmium in CdS is greater than that for sulphur [58].

(2) The observed whisker growth points out that Cd is transported on the surface of the overgrown CdS film where it reacts with the sulphur.

(3) As mentioned above the CdS layers repeated the surface structure of the cadmium single crys-

tals. Evidently the cadmium surface was blocked by the CdS thin film formed in the first moment of the sulphur introduction. For further growth of the CdS layer cadmium ions have to diffuse through this film (see also [52]). Otherwise, if the sulphur diffuses through the CdS/Cd interface, the latter has to penetrate the bulk of the cadmium single crystal and may change its form.

The lattice parameters of the CdS layers calculated from the X-ray and electron diffraction patterns were $a = 4.13 \pm 0.01$ Å and $c = 6.70 \pm 0.01$ Å. The a value agrees well with the data in the literature, while the c value is smaller as compared with the data in the literature [59].

Acknowledgements

The authors are grateful to Academician R. Kaischew for his interest. Gratitude is expressed to Dr I. Tomov for some help with the X-ray diffraction studies. Thanks are also due to Mrs B. Urutcheva for her technical assistance.

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Received 9 August and accepted 24 October 1977.