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AES investigation of the composition of polar $\{0001\}$ surfaces of CdS

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The composition of polar $\{0001\}$ surfaces of CdS was investigated by Auger electron spectroscopy. Both the A (0001) or cadmium face and the B $(000\bar{1})$ or sulphur face showed sulphur enrichment. This enrichment is attributed to the forward scattering of sulphur below the surface and the subsequent exposure of these atoms through continued sputtering. The effect of carbon contamination on the S/Cd ratio on both faces was investigated. The decrease of this ratio with increased carbon contamination is explained in terms of differences in the escape depths of the sulphur and cadmium Auger electrons.

1. Introduction

Cadmium sulphide, an n-type semiconductor, exists in two crystalline modifications: the hexagonal (wurtzite) and the cubic (sphalerite) structures [1]. The wurtzite modification has atoms tetrahedrally bound in network arrangements as shown in Fig. 1a. The close packed sulphur anion lattices have one octahedral site and two tetrahedral sites per anion with the cadmium cations occupying half of the tetrahedral sites in the hexagonal close-packed lattice. The crystal does not have a centre of symmetry and there is a polar axis parallel to the c-axis, i.e., the [0001] direction. Alternate $\{0001\}$ layers in this structure are composed of cadmium and sulphur ions, respectively, with each layer arranged in a close packed manner, as shown in Fig. 1b. Chemical-etch patterns, evaporation rates, as well as voltage–current and voltage–capacitance characteristics in Cu_2S–CdS junction solar cells have been found to be distinctly different on the two polar basal planes [2–5]. In this paper we report the results of an investigation on the composition of these two polar surfaces and the influence of contaminants on composition as determined through Auger electron spectroscopy (AES) techniques.

2. Experimental procedure

Cadmium sulphide single crystals of ultra-high purity supplied by the Eagle-Picher Company of Miami, Oklahoma, were used in this research. The crystals were 2 mm thick, irregularly shaped wafers with nominal resistivities in the range of 1 to 10 Ω cm. The crystals were pre-oriented along the c-axis, with large surfaces parallel to the basal plane. The deviation from this orientation was within 0.5°.

The polar (0001) and $(000\bar{1})$ surfaces of a CdS single crystal can be identified by using a chemical-etch technique [2]. The etching solution was prepared by mixing six parts by volume of concentrated nitric acid, six parts by volume of glacial acetic acid, and one part by volume of distilled water. Treated with this solution, the cadmium (0001) face exhibited characteristic hexagonal etch pits while the sulphur $(000\bar{1})$ face exhibited non-distinct hillocks separated by narrow valleys. These faces are commonly referred to as the A (or cadmium) and B (or sulphur) face.

After the surface identification, each crystal was cut into two pieces by fracturing along a groove inscribed on the surface. The crystals were then successively polished by using 600 grit sand paper, 0.3 and 0.05 µm alumina powder. After cleaning by acetone and distilled water, the crystals were transferred to a sample stud and loaded into the vacuum system.

Clean surfaces can be produced by cleaving single crystals or by ion bombardment in ultrahigh vacuum. Since the polar, $\{0001\}$, surfaces of CdS are not the cleavage surfaces, clean surfaces were obtained by ion bombardment. Ion bombardment, however, can create lattice strain as had been demonstrated by Brillson for the Al–Si interface [6]. For this reason, clean surfaces were produced in this study by first using 2 kV argon ion-beam rastering on the sample surface to remove the contaminants and then by annealing the surface through ion sputtering at low accelerating potential (0.65 kV). This technique has been shown to produce clean, relatively stain-free surfaces [7].

The experimental apparatus used in this investigation consisted of an ultrahigh vacuum system which was made up of two components: a preparation chamber and an (AES) analysis chamber. A sample introduction device allowed for the transfer of samples between these chambers directly. The stainless steel preparation chamber was evacuated by a Leybold-Heraeus (model TMP150) turbomolecular pump which provided a base pressure of 10^{-9} torr. The analysis chamber, a Perkin-Elmer TNB-X ultrahigh

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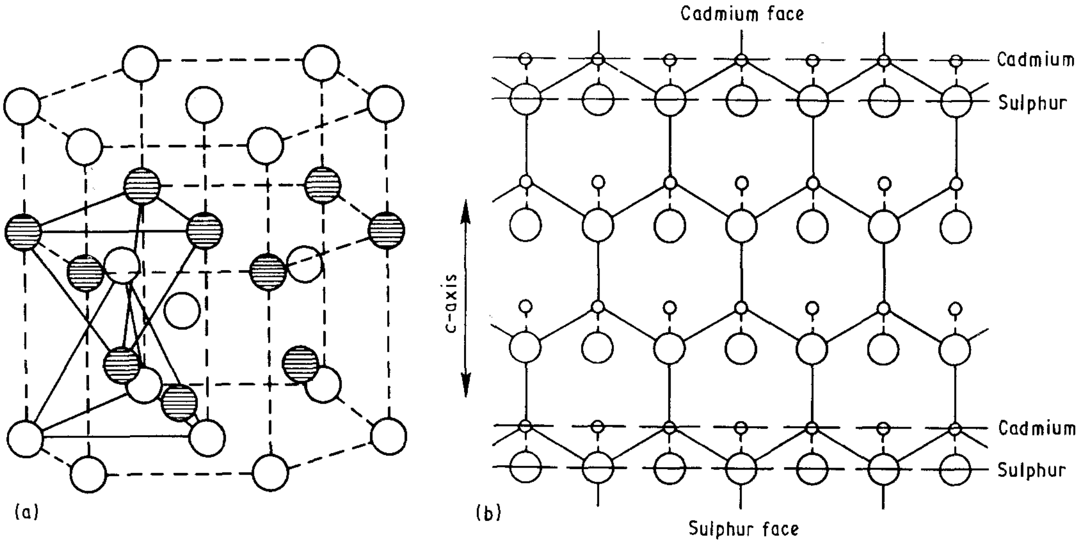

Figure 1 (a) Tetrahedral sites in the Wurtzite structure of CdS. Hatched and open circles represent sulphur and cadmium atoms, respectively. (b) Arrangements of layers of sulphur and cadmium atoms on polar {0001} surfaces of CdS.

vacuum system, was pumped by eight 25 l sec^{-1} differential ion pump elements which provided a base pressure of $< 5 \times 10^{-10}$ torr. The chamber contained a double-pass cylindrical mirror analyser (CMA) and a differential sputtering ion gun.

Crystals were loaded into the preparation system from a loading cross. Through the use of a sample transfer probe (made by UHV Instruments, of Buffalo, New York) the sample can be transferred back and forth between the loading cross, the preparation chamber, and the analysis chamber. Transfer between the preparation and analysis chambers was not made until the pressure in the former had decreased to below 10^{-7} torr. At this point the gate valve between the two chambers is opened and the sample stud containing the crystals is transferred to the carousel in the analysis chamber. After retracting the sample transfer probe the gate valve was closed and the crystals were positioned in front of the Auger cylindrical mirror analyser. A beam energy of 3 kV and a beam current of 5 μA were selected to obtain the Auger spectra in this study.

A typical Auger spectrum of an as-polished surface is shown in Fig. 2. Peaks of contaminants (carbon, oxygen, and chlorine) as well as those of cadmium and sulphur were observed. The crystals were then sputter-cleaned by an argon ion beam. The initial conditions for this process were set at 25 mA emission current and 2 kV beam voltages. A raster size of 10 × 10 mm was used to sputter the surfaces for 30 min under these conditions. After the completion of this step, the beam voltage was reduced to 0.65 kV and the process was continued for an additional 2 h to anneal the crystals [7]. The argon flow rate was controlled such that a pressure of 20×10^{-3} atm is maintained in the ionization chamber.

3. Results and discussion

3.1. Non-stoichiometry of the crystal surfaces

As the sputtering process of the as-polished samples is initiated, the Auger signal intensities for cadmium and sulphur increase while those of adsorbed carbon, oxygen and chlorine decrease with an increase in the thickness of the removed surface layer. The carbon peak shape (Fig. 2) is identical to that of graphite, indicating that the carbon present on the surface of CdS is a result of the decomposition of residual, carbon-containing gases such as CO, CO_2, hydrocarbons, etc. A weak signal of argon was also observed in the spectra at the outset of the ion etching. The ratio of the sulphur to cadmium (S/Cd) peak intensities continuously increased as the surface layers were removed. The concentrations on the completely cleaned surfaces have been calculated to correspond to a range of atomic compositions of 47 to 49% Cd and 53 to 51% S, indicating a preferential sulphur accumulation at the surfaces. These results showed no significant difference between the (0001) or A and (000$\bar{1}$) or B faces of CdS. An example of an Auger spectrum of a sputter-cleaned surface is shown in Fig. 3.

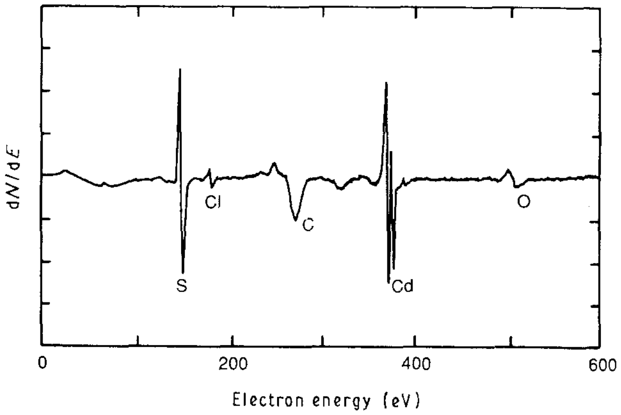

Figure 2 Auger spectrum of as-polished {0001} CdS surfaces (3 kV, 35 μA, $E/M = 2200$ V, $T/C = 0.3$ sec, $S = 10\,X$, P–P = 3 eV).

Brillson [8] has used the S/Cd peak-to-peak Auger intensity ratio of the cleaved prismatic (11$\bar{2}$0) surface as a gauge to calibrate the relative non-stoichiometries of other CdS surfaces. The atoms in the non-polar (11$\bar{2}$0) plane are held by three bonds within and below the surface while only one bond of equal strength

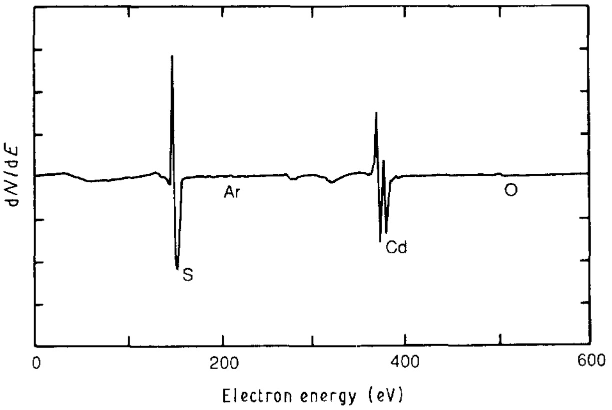

Figure 3 Auger spectrum of sputter-cleaned {0001} surfaces of CdS (3 kV, 35 μA, $E/M = 1900$ V, $T/C = 0.3$ sec, $S = 10\,X$, P–P = 3 eV).

extends outward and thus non-stoichiometric cleavage in this plane is highly unlikely. The Auger spectrum for a 1 keV ion-bombarded $(11\bar{2}0)$ surface exhibited a non-stoichiometry of 48% Cd against 52% S. As an additional comparison, pulse counting of the undifferentiated Auger spectrum was obtained whose peak height ratio yielded a non-stoichiometry of 45% Cd against 55% S for the sputtered surface [8]. Although different orientations of the CdS crystal were used in the present investigation, the existence of sulphur-rich ion-bombarded surfaces are in agreement with the results of Brillson [8].

This deviation from stoichiometry is independent of prior surface treatment, indicating that the difference in the sputtering yield of cadimum and sulphur induces the selective etching of the CdS crystal surfaces and makes the surfaces sulphur-rich. Several mechanisms have been proposed to explain the selective sputtering phenomenon [9]. Direct energy transfer from the incident particles to the surface atoms would cause an enrichment in the heavier component. Thermal sputtering, due to a thermal spike, would cause targets to be enriched by components with lower vapour pressures. Neither of the above mechanisms can explain the observations of surface sulphur enrichment satisfactorily. Energy transfer considerations would favour the enrichment of the surface by the heavier element, cadmium. Similarly, the effect of thermal sputtering (if it can lead to non-congruent evaporation) is an enrichment of the surface by the less volatile component, cadmium [10].

The diffusion of sulphur from the bulk to the surfaces of CdS has been observed [8]. Such a process leaves sulphur interstitials at the surfaces and sulphur vacancies a few atomic layers below. A mechanism involving the out-diffusion of sulphur would be consistent with the detected higher concentrations of sulphur on the {0001} surfaces of CdS. However, sulphur interstitials have been observed only on prismatic and B $(000\bar{1})$ basal planes of polished and etched CdS in UHV [11]. This does not, therefore, explain the sulphur enrichment on both the A (Cd) and B (S) surfaces observed in this study. It is likely, therefore, that the sulphur enrichment on both polar surfaces is due to the forward scattering (knock-on effect of ion sputtering) of the sulphur component. Sigmund [12] has pointed out that enrichment of lighter components can result if the sample is exposed to very high doses. A sequence of events in which a layer rich in light atoms is first created below the surface by forward scattering and then is exposed by subsequent sputtering can lead to the observed surface enrichment of the light element.

3.2. Effect of surface contaminations on non-stoichiometry

In order to determine the influence of the surface-adsorbed impurities on the S/Cd peak intensity ratio, a sputter-cleaned CdS crystal was exposed to different levels of vacuum for varying lengths of time. The spectrum of this clean crystal, shown in Fig. 3, was used as a reference. When the crystal was left in the analysis chamber for one day under a background pressure of $< 10^{-9}$ torr, the Auger spectrum at the end of this period was essentially unchanged, as seen in Fig. 4. The crystal was then transferred back to the preparation chamber (10^{-8} torr) and left there for five days. An Auger spectrum obtained at this point is shown in Fig. 5. Following this, the crystal was brought up to atmosphere for an hour, reloaded into the analysis chamber and a spectrum was obtained as shown in Fig. 6. The crystal was then removed from the analysis chamber and stored under atmospheric conditions overnight. A spectrum obtained at the end of this treatment is shown in Fig. 7. The instrumental parameters for the Auger spectra referred to above are indicated on each figure. The peak-to-peak height of sulphur and cadmium peaks and the S/Cd intensity ratios were calculated and are listed in Table I for the conditions described above.

No carbon peak was found on the spectrum of the sample left for one day in the analysis chamber, and the intensities of both sulphur and cadmium peaks decreased only slightly relative to those obtained on the sputter-cleaned surfaces (Fig. 4). After five days in the preparation chamber under a pressure of 10^{-8} torr, the sample exhibited a carbon peak and a small chlorine peak (Fig. 5). The sulphur and cadmium peak amplitudes, as well as the S/Cd intensity ratio had decreased relative to the corresponding

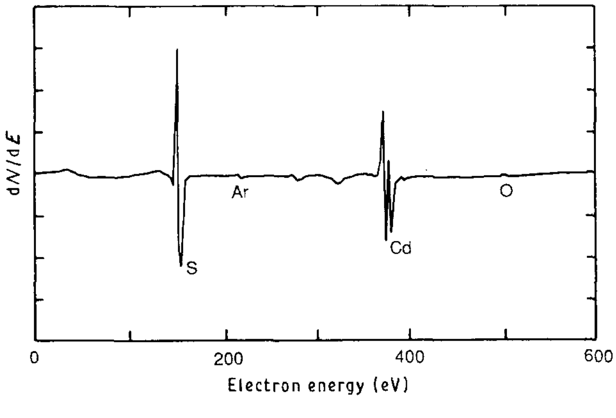

Figure 4 Auger spectrum of {0001} surface of CdS crystal left in the analysis chamber (pressure $< 10^{-9}$ torr) for one day (3 kV, 35 μA, $E/M = 1900$ V, $T/C = 0.3$ sec, $S = 10\,X$, P–P = 3 eV).

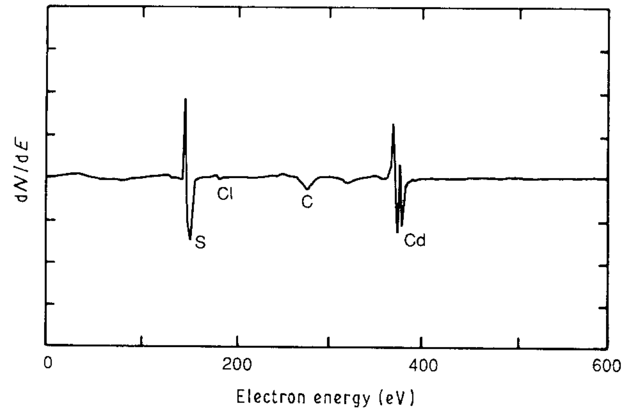

Figure 5 Auger spectrum of {0001} surface of CdS crystal left in the preparation chamber (pressure $\sim 10^{-9}$ torr) for five days (3 kV, 35 μA, E/M = 1900 V, T/C = 0.3 sec, S = 10 X, P–P = 3 eV).

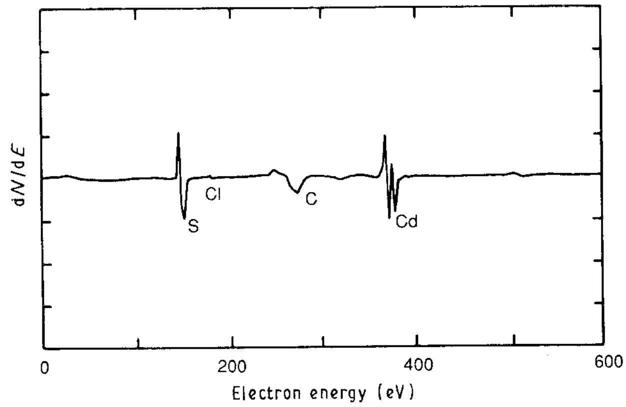

Figure 6 Auger spectrum of {0001} surface of CdS crystal exposed to room atmosphere for one hour (3 kV, 35 μA, E/M = 1900 V, T/C = 0.3 sec, S = 10 X, P–P = 3 eV).

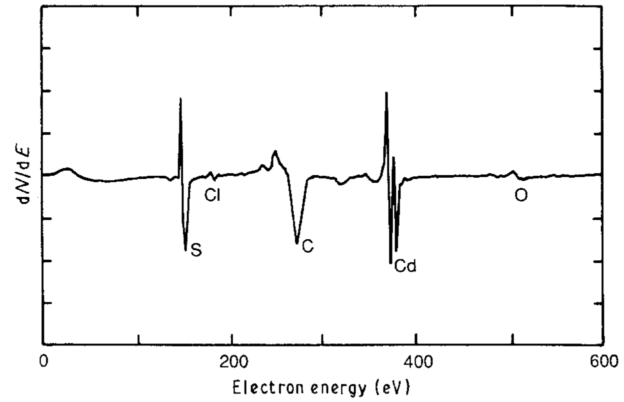

Figure 7 Auger spectrum of {0001} surface of CdS crystal exposed to room atmosphere for one day (3 kV, 35 μA, E/M = 2200 V, T/C = 0.3 sec, S = 10 X, P–P = 3 eV).

TABLE I Auger peak-to-peak heights and S/Cd peak intensity ratios on {0001} surfaces of CdS. (Electron multiplier voltage = 1900 V)

Sample condition (treatment)	Peak Heights (arb. units)		S/Cd	Figure
	Sulphur	Cadmium		
Sputter cleaned	13.1250	7.8857	1.6644	3
In UVH (1 day)	12.7002	7.8857	1.6348	4
In HV (5 days)	8.4521	6.4990	1.3006	5
In air (1 h)	5.1416	4.9512	1.0384	6
In air[a] (1 day)	9.0918	10.2197	0.8896	7

[a] Electron multiplier voltage = 2200 V.

values obtained on a sputter-cleaned surface. The carbon peak became stronger, the sulphur and cadmium peaks became weaker, and the S/Cd intensity ratios decreased as the quality of the vacuum became worse. While the chlorine signal remained nearly constant, a small oxygen peak developed (Fig. 7). The trend in the sulphur and cadmium peak intensities even reversed, with the peaks becoming stronger after the crystal was left under atmospheric conditions overnight. No new lines, associated with chemical shifts, were observed. Since chlorine and oxygen existed only in trace amounts, the change of the S/Cd intensity ratio is believed to be caused by the adsorption of carbon.

A decrease of the S/Cd intensity ratio had been reported by Brillson on an oxygen-adsorbed CdS ($11\bar{2}0$) surface [13]. In that study, surface contamination by oxygen was achieved by placing a cleaved surface ~ 2.5 cm from a heated (1800 °C) tungsten filament for 15 min at an oxygen pressure of 10^{-5} torr. No other chemical species were adsorbed as a result of this treatment. The decrease of the S/Cd intensity ratio was explained in terms of the oxygen atom either replacing or shadowing (covering) sulphur atoms preferentially on this surface [13]. Since the polar surfaces of CdS single crystal are composed predominantly of either cadmium or sulphur, the preferential shadowing cannot account for the change in the S/Cd ratio on both surfaces. Also, since no chemical reaction is expected between CdS and carbon at room temperature, a possible explanation for the present observations focuses on the escape depth for the sulphur and cadmium Auger electrons. Assuming the escape depth is a minimum near an energy E of 60 eV and increases approximately as $E^{1/2}$ from 100 to 2000 eV [14], the characteristic sulphur LMM peak at 152 eV has an escape depth of ~ 0.6 nm while that of cadmium MNN peak at 376 eV has an escape depth of ~ 1 nm. Thus it is possible that upon exposure to carbon the sulphur peak is more affected than the cadmium peak because of the smaller escape depth associated with it. The necessity for more than a 5 nm thick surface layer to be removed before a clean surface can be reobtained, a value that is much greater than the escape depth of either sulphur or cadmium Auger electrons, leads to the speculation of two possibilities. The observations can be explained either by a non-uniform coverage of the contaminants on the surfaces or by a nonstoichiometric outdiffusion of cadmium and sulphur components through the adsorbed carbon layers.

After the crystal surface is cleaned by ion etching, the vacancy and interstitial concentrations near the surface can exceed their bulk equilibrium values due to beam damage. This surface disorder can promote the interdiffusion by vacancy and interstitial mechanisms [15]. Brillson had suggested annealing the CdS ($11\bar{2}0$) crystals at 400 °C for 4 h to obtain an ordered

LEED pattern [8]. Such annealing must be carried out in an oxidant-free environment to prevent formation of an insulating interface. Morimoto [7] had suggested an alternative method to etch the surfaces with 2 kV argon sputtering ion beam and then reduce the accelerating potential to 0.65 kV for several minutes instead of ordinary thermal annealing. In an attempt to select the proper technique to anneal the crystals, S/Cd intensity ratios were measured as an indication of the effectiveness of the annealing processes. Thermal annealing and several different low energy ion beam annealing processes were evaluated. A small decrease of the S/Cd intensity ratio was observed for all annealing techniques, indicating a reduction in non-stoichiometry. No significant differences were, however, found among the different processes. Due to the possibility of having extensive facet formation [16] and sulphur sublimation from the surfaces by thermal annealing [17], low energy sputter-anneal technique was selected for this study, as discussed earlier.

4. Conclusions

The conclusions are as follows.

(1) Argon ion sputtering causes a selective etching of cadmium on the CdS crystal basal surfaces. While the diffusion of sulphur from the bulk to the surface of CdS may account for the excess sulphur on the B $(000\bar{1})$ face, the sulphur-rich non-stoichiometry of both polar surfaces is probably due to the forward scattering of the sulphur component below the surface, followed by the exposure of the sulphur atoms through subsequent sputtering.

(2) The observed decrease in S/Cd concentration ratios with the carbon contamination layers is suggested to be the result of different escape depths of the sulphur and cadmium Auger electrons.

Acknowledgements

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