

Surface characterization of CdS_{0.62}Se_{0.38} by X-ray photoelectron spectroscopy

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Cadmium chalcogenides are miscible among themselves to give solid solutions. CdS and CdSe form a continuous series of solid solutions among themselves. The bandgap energy varies linearly with the composition of the solid solution [1-3]. Several reports on the photoelectrochemical properties of these solid solutions are available [4-10]. Noufi *et al.* [7] prepared CdS_{1-x}Se_x by sintering a mixture of CdS and CdSe in the required composition and by vacuum deposition. They reported that the bandgap of the solid solution varied monotonically with the composition. The photoassisted oxidation of sulphide with these solid solutions as the photoanodes showed that the flatband potentials of the solid solutions are more negative than that of CdS, thus making them more suitable photoanode materials for solar energy conversion. It is known that CdS_{0.62}Se_{0.38} (PC) is more stable towards photo-corrosion than CdS [11]. The surface properties of these solid solutions vary depending on the method of preparation. It is necessary to know the surface properties of these solid solutions in order to understand their photoelectrochemical as well as photocatalytic behaviour [12]. A detailed study of the surface properties of these materials has not been reported. Hence, a detailed X-ray photoelectron spectroscopic (XPS) investigation on one of the representative compounds (CdS_{0.62}Se_{0.38}) of the series of CdS-CdSe solid solutions was undertaken in this study.

CdS (Fluka, 99.999% purity) and CdSe (Koch-Light, 99.999% purity) were taken in the required composition. The mixture was ground well in acetone and the homogenized mixture was allowed to dry at room temperature and was pressed into pellets of 12 mm diameter. The pellets were sintered in flowing nitrogen for 4 h.

The X-ray diffraction patterns of CdS, CdSe and PC were recorded on a Philips Generator PW 1140 X-ray diffractometer using a Cu K α X-ray source and nickel filters. From the experimentally observed diffraction angles (θ), the interplanar spacings (d -values) were calculated. These d -values were used to calculate the lattice parameters.

XPS studies were made with an ESCA Lab Mk 11 (VG Scientific Co., UK) X-ray photoelectron spectrometer at a pressure of 1×10^{-7} Pa on sintered PC pellets before and after sputtering the sample with argon ions. The X-ray source used was Al K α with an energy of 1486.6 eV. The carbon 1s XPS peak at 285.0 eV was used as the internal standard. The

argon ion sputtering was carried out at 20 μ A for different times.

The d -values obtained from the X-ray diffractograms of CdS and CdSe match well with those reported for the hexagonal modifications of CdS and CdSe. The lattice parameters (Table I) agree well with those reported in the literature [13], showing that the cadmium chalcogenides used in this investigation were in the hexagonal form. The lattice parameters of PC lie between those of CdS and CdSe (Table I), indicating that PC is in a state of solid solution, crystallizing in the hexagonal form. Thus, X-ray diffraction study, which is a bulk characterization technique, reveals the formation of the solid solution. To discover more about the surface of PC, XPS studies were carried out.

From Fig. 1 it can be seen that the Cd 3d XPS

TABLE I Lattice parameters of CdS, CdSe and CdS_{0.62}Se_{0.38}

Material	Lattice parameters	
	a (nm)	c (nm)
CdS hexagonal	0.4134 (0.4136)	0.6700 (0.6713)
CdSe hexagonal	0.4301 (0.4299)	0.7016 (0.7010)
CdS _{0.62} Se _{0.38} hexagonal	0.4113	0.6899

Reported values [13] are given in parentheses.

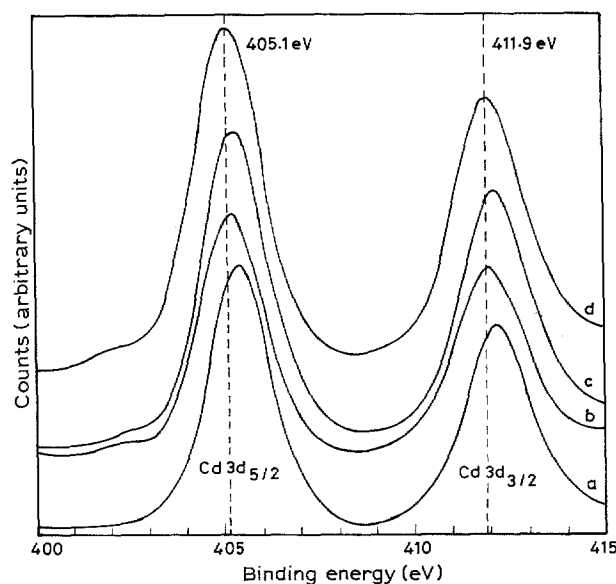


Figure 1 Cd 3d XPS peaks of CdS_{0.62}Se_{0.38} (a) before argon ion sputtering, and after argon ion sputtering for (b) 1 min, (c) 15 min and (d) 39 min.

peaks shift to lower binding energy. The peak areas increase with the argon ion sputtering time, indicating that the amount of Cd present increases while moving from the surface into the bulk. The binding energies of the Cd 3d XPS peaks reported [14] for CdS and CdSe are close to each other (Cd 3d_{5/2} 405.00 and 405.13 eV and Cd 3d_{3/2} 411.80 and 411.93 eV, respectively) [15], but the binding energy values reported for CdS are lower than those reported for CdSe [14]. Hence, the shift in the XPS peaks towards lower binding energy (Fig. 1) can be attributed to the presence of more CdS in the subsurface of PC. Similar shifts observed in the case of Cd 4d XPS peaks (Fig. 2) also suggest the segregation of CdSe to the surface. The decrease in the peak areas of Se 3p_{1/2} peaks on argon ion sputtering (Fig. 3) clearly shows that the concentration of CdSe is greater than the subsurface concentration of CdSe. The Se 3p_{1/2} peak area remains constant after 15 min argon ion sputtering, showing that the concentration of CdSe is constant in the bulk of PC. This agrees with the conclusion arrived at from the X-ray diffraction studies. As the Se 3p_{1/2} XPS area is decreasing with increasing argon ion sputtering time, the Se 2p_{3/2} XPS peak area will also decrease and the ratio of the areas of the Se 3p_{1/2} and 3p_{3/2} XPS peaks should be 1:2 (for the p-orbital, $l = 1$, therefore, $2l:(2l + 2) = 1:2$) [16]. So by subtracting twice the area of the Se 3p_{1/2} XPS peak from the peak area of the broad XPS peak around 160 eV (Fig. 3), which comprises the S 2p_{1/2}, 2p_{3/2} and Se 3p_{3/2} XPS peaks, one can obtain the peak area of the S 2p XPS peak area alone.

From Table II it is evident that the S 2p peak area increases with argon ion sputtering time (the increase in the peak areas of the broad peaks around

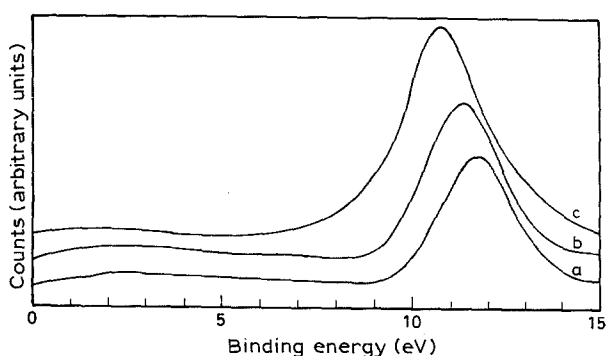


Figure 2 Cd 4d XPS peaks of CdS_{0.62}Se_{0.38} (a) before argon ion sputtering, and after argon ion sputtering at 20 μ A for (b) 1 min and (c) 39 min.

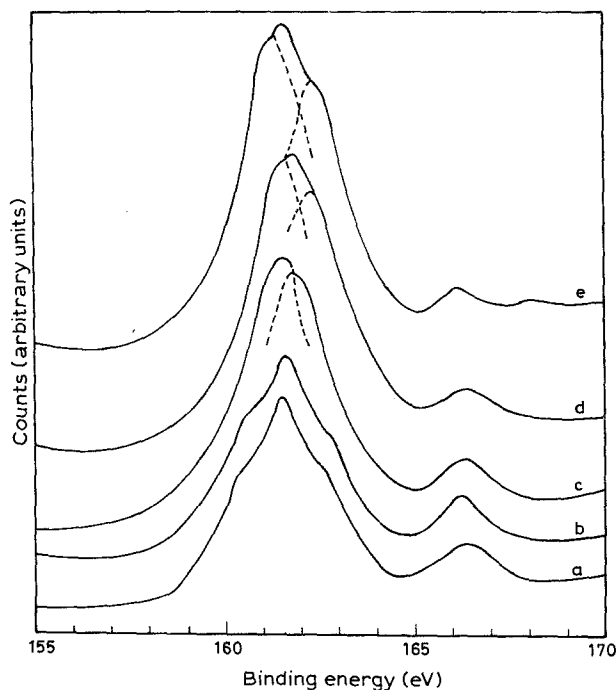


Figure 3 S 2p and Se 3p XPS peaks of CdS_{0.62}Se_{0.38} (a) before argon ion sputtering, and after argon ion sputtering at 20 μ A for (b) 1 min, (c) 5 min, (d) 15 min and (e) 39 min.

160 eV in Fig. 3 should be due to the increase in the S 2p XPS peak areas only as the Se 3p_{3/2} XPS peak area decreases with the argon ion sputtering time), indicating that the subsurface layers of PC contain more CdS than the surface layers.

From Table III and Fig. 3 it can be seen that the observed positions of the S 2p and Se 3p XPS peaks agree fairly well with those reported [14, 15] for CdS and CdSe. It is also evident that the S 2p XPS peak areas are greater than those of the Se 3p XPS peaks before and after argon ion sputtering for different time intervals, indicating that in PC the S content is greater than that of Se, on the surface as well as in the subsurface layers. This is in agreement with expectations, because the amount of CdS present in PC is more than that of CdSe per the composition of the solid solution. However, while moving from the surface of PC into the subsurface layers (achieved by argon ion sputtering) the Se/S ratio decreases, as evidenced by the decrease in the Se 3p and the increase in the S 2p XPS peak areas with increasing argon ion sputtering time (Table II). Also, at every stage of argon ion sputtering the overall S content is greater than that of Se (Table II). This confirms that the relative amount of CdSe present on the surface is

TABLE II Peak areas of the S 2p and Se 3p XPS peaks of CdS_{0.62}Se_{0.32}

Argon ion sputtering time at 20 μ A min ⁻¹	XPS peak areas (cm ²)			
	(S 2p + Se 3p _{3/2}) Observed, A	Se 3p _{1/2} Observed, B	Se 3p _{3/2} Calculated, C	S 2p A - C
0	13.04	1.98	3.96	9.08
1	13.16	1.31	2.62	10.58
5	17.37	1.25	2.25	15.12
15	18.50	0.75	1.50	17.00
39	20.40	0.77	1.54	18.86

TABLE III Binding energies of the S 2p and Se 3p XPS peaks of CdS_{0.62}Se_{0.32}

Argon ion sputtering time at 20 $\mu\text{A min}^{-1}$	Binding energies of XPS peaks (eV)			
	S 2p _{1/2}	S 2p _{3/2}	Se 3p _{1/2}	Se 3p _{3/2}
0	162.7	161.5	166.4	160.3
1	162.9	161.6	166.2	160.5
5	162.2	161.5	166.3	160.1
15	162.4	161.8	166.3	160.1
39	162.5	161.5	166.2	160.9
Reported [14] for CdS and CdSe	162.72	161.60	166.04	160.32

more than that present in the subsurface layers, and the reverse is true for CdS. As the melting point of CdSe (1530 K) is lower than that of CdS (2020 K), it is reasonable to expect CdSe to segregate to the surface while sintering (923 K) during the preparation of the solid solution. From Figs 2 and 3 and Table III it is clear that argon ion sputtering does not alter the binding energies of the Cd 3d, 4d, S 2p and Se 3p XPS peaks, indicating that argon ion sputtering does not affect the oxidation state of Cd, S and Se in PC.

In conclusion, XPS studies on PC show the segregation of CdSe to the surface. As the melting point of CdSe is lower than that of CdS, the former segregates to the surface while sintering the mixture of CdS and CdSe during the preparation of the solid solution. Argon ion sputtering aids the removal of the surface layers without affecting the oxidation states of Cd, S and Se in PC.

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