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X-ray photoelectron spectroscopic studies on Pd/CdS

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Metallized CdS is used as a photocatalyst for many reactions and as a photoanode in photoelectrochemical (PEC) cells [1–4]. Conversion and storage of solar energy can be achieved by means of photocatalysis as well as by PEC cells. The photocatalytic and photoelectrochemical properties of metallized CdS depend on its surface properties. Pd/CdS is a better photocatalyst and photoanode than CdS [3]. However, a detailed surface study of Pd/CdS is lacking. X-ray photoelectron spectroscopy (XPS) is a versatile tool to probe the surface of materials. XPS investigation of Pd/CdS will yield useful information such as the oxidation state of Pd, the contact between Pd and CdS, and other species present on the surface. Metallized CdS is mostly prepared by the photodeposition of noble metals [1, 3, 4]. Therefore, in the present investigation Pd, one of the representatives of noble metals, was photodeposited on CdS and the Pd/CdS obtained was analysed by XPS.

Pd, Pt, Rh, Ru and Ni/CdS were prepared by the simultaneous photodeposition (illuminating for 15 min with a 1000 W tungsten–halogen lamp) of these metals on a sintered (4 h at 873 K in nitrogen) CdS (Fluka, 99.999% purity) pellet from an equimolar (1×10^{-4} M) solution (acetic acid, pH 4.5) of the corresponding metal chlorides. Following a similar procedure, Pd was photodeposited from a solution of $PdCl_2$ (Arora Mathey Ltd, India). After photodeposition the pellets were washed with triply distilled water and dried in air at room temperature (303 K). The sides of the pellets that were exposed to visible light during the photodeposition were subjected to XPS analysis.

The XPS studies were made with an ESCA Lab Mk II (VG Scientific Co., UK) at room temperature and at a pressure of 1×10^{-7} Pa before and after sputtering with argon ions. The X-ray source used was MgK_α with an energy of 1253.6 eV. The C 1s peak at 285.0 eV was used as the internal standard.

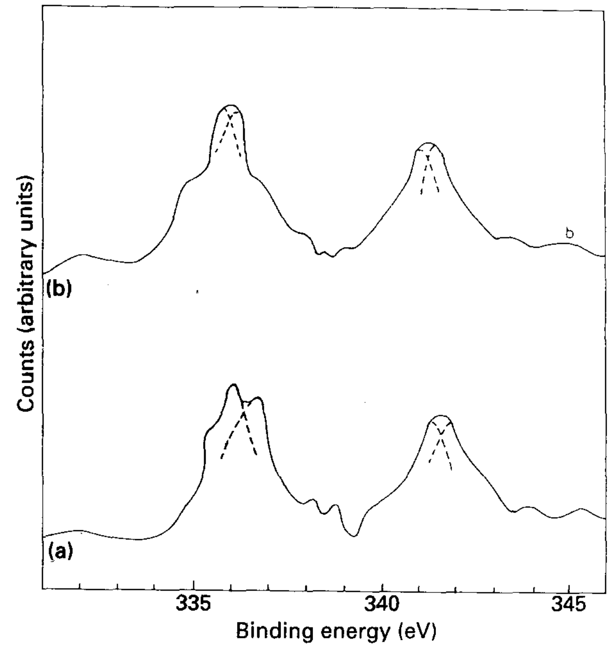

Figure 1 Pd 3d XPS peaks of Pd, Pt, Rh, Ru and Ni/CdS: (a) before argon-ion sputtering and (b) after sputtering with argon ions at 75 μA for 8 min.

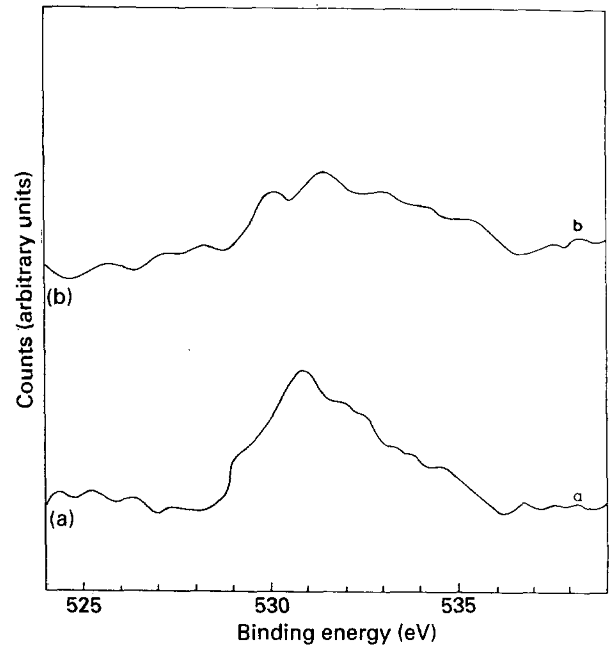

Figure 2 O 1s and Pd 3p XPS peaks of Pd, Pt, Rh, Ru and Ni/CdS: (a) before argon-ion sputtering and (b) after sputtering with argon ions at 70 μA for 8 min.

In the cases of Pd, Pt, Rh, Ru and Ni/CdS prepared by the simultaneous photodeposition of these metals, the Pd 3d and 3p binding energies (Figs 1 and 2) are higher than those reported for Pd metal, viz. 344.7, 340.0 and 531.5 eV [5], indicating that Pd which is on the surface of CdS is not in the zero oxidation state. The several Pd–O species identified are shown in Table I. Hence, in the case of Pd/CdS the XPS spectra were recorded only after argon-ion sputtering, in order to study the surface free of oxide layer. From Fig. 3 it is evident that with an increase in the time of argon-ion sputtering the intensities of the Pd 3d XPS peaks decrease and the binding energies of the Pd 3d electrons shift towards the

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TABLE I Various Pd–O species present on the surface of Pd, Pt, Rh, Ru and Ni/CdS

Energy level of the elements probed	Binding energy (eV) Observed	Binding energy (eV) Reported	Species assigned
Before argon-ion sputtering			
Pd			
$3d_{3/2}$	341.8	341.7 [6, 7]	PdO
$3d_{5/2}$	336.5	336.4 [6, 8]	PdO
$3p_{3/2}$	532.5	532.7 [8]	PdO
O			
1s	529.3	529.3 [8]	PdO
Pd			
$3d_{5/2}$	335.5	a	PdO_x ($x < 1$)
$3d_{5/2}$	338.1	337.9 [8]	PdO_2
$3d_{3/2}$	343.9	b	PdO_2
$3p_{3/2}$	534.7	534.3 [8]	PdO_2
$3d_{5/2}$	336.7	c	PdO_{2-x} ($1 < x < 2$)

[a] The binding energy value lies between those reported for Pd and PdO, indicating the formation of PdO_x ($x < 1$).

[b] A positive shift of 3.5 eV in the binding energy shows the presence of Pd^{2+}.

[c] The binding energy value lies between those reported for PdO and PdO_2, implying the presence of PdO_{2-x} ($1 < x < 2$).

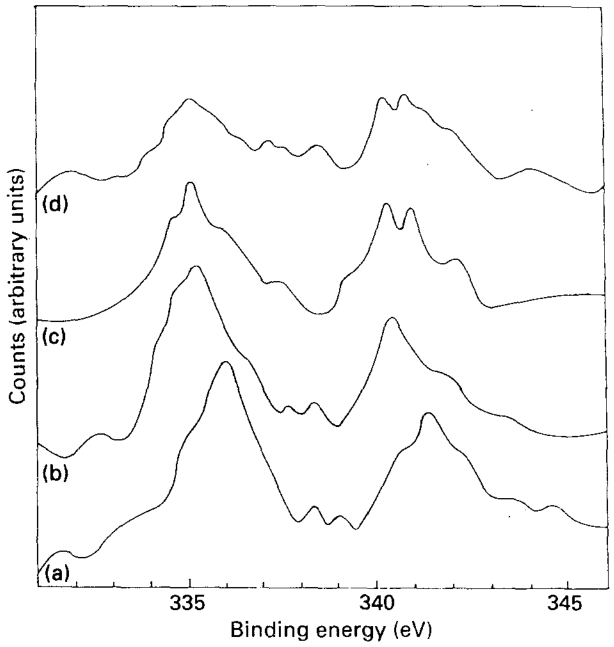

Figure 3 Pd 3d XPS peaks of Pd/CdS at different argon-ion sputtering times (at 50 μA): (a) 14.0, (b) 44.0, (c) 75.2 and (d) 113.6 min.

values reported for Pd metal, viz. 334.7 and 340.0 eV [5]. After a sputtering time of 75.2 min at 50 μA, the Pd metal peaks (334.7 and 340.0 eV) start to appear (Fig. 3) and after a sputtering time of 113.6 min it is found that the observed binding energies of Pd 3d and 3p electrons (Figs 3 and 4) agree with those reported for Pd metal (Table II), indicating the presence of Pd metal. Furthermore, from Fig. 4 it is seen that the intensity of the O 1s XPS peak decreases with increasing argon-ion sputtering time, indicating the removal of surface oxide layers. From Table III it can be observed that the intensities (heights) of the Cd 3d and S 2p XPS peaks increase with argon-ion sputtering of Pd/CdS, as argon-ion sputtering removes surface oxide layers. Even after a sputtering time of 113.6 min some oxide still remains on the surface (Figs 3 and 4 and Table II). Thus, the XPS studies imply that the photodeposited Pd which is in the zero oxidation state is oxidized upon exposure to the atmosphere (air). The amount of the different Pd–O species present decreases with the extent of depth profiling (Figs 3 and 4) and the Pd metal peaks appear as the top few layers are removed by argon-ion sputtering. This shows that the Pd is oxidized to a certain depth of the sample only, and the Pd present in the subsurface layers is not oxidized as the surface oxide layer prevents further oxidation.

TABLE II Different Pd species present on the surface of Pd/CdS after argon-ion sputtering

Energy levels of the elements probed	Binding energy (eV) Observed	Binding energy (eV) Reported	Species assigned
After 113.6 min argon-ion sputtering at 50 μA			
Pd			
$3d_{5/2}$	334.7	334.6 [5]	Pd
$3d_{3/2}$	340.4	340.1 [5]	Pd
$3p_{3/2}$	531.7	531.5 [5]	Pd
$3p_{3/2}$	532.8[c]	532.7 [8]	PdO
$3p_{3/2}$	534.3[c]	534.3 [8]	PdO_2
$3p_{3/2}$	532.2[c]	a	PdO_x ($x < 1$)
$3p_{3/2}$	533.3[c]	b	PdO_{2-x} ($1 < x < 2$)

[a] The binding energy value lies between those reported for Pd and PdO, indicating the formation of PdO_x ($x < 1$).

[b] Low-intensity peaks (Figs 2 and 3).

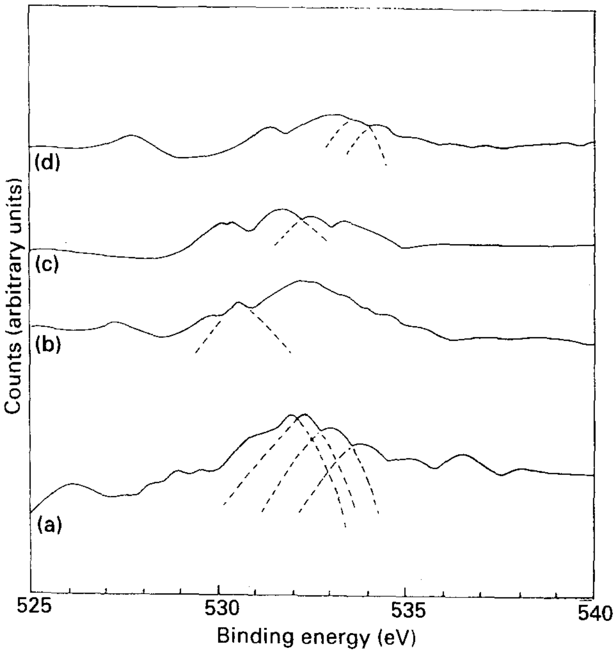

Figure 4 O 1s and Pd 3d XPS peaks of Pd/CdS at different argon-ion sputtering times (at 50 μA): (a) 14.0, (b) 44.0, (c) 75.2 and (d) 113.6 min.

On n-type semiconductors (e.g. n-CdS) reduction reactions such as $Pd^{2+} + 2e^- \rightleftharpoons Pd$ occur on the dark side of the semiconductor [9]. However, the photodeposition of Pd on the illuminated face of CdS

TABLE III X-ray photoelectron spectroscopic data on Pd/CdS

Energy levels of the elements probed	After 14 min Ar^+ sputtering at 50 μA		After 113.6 min Ar^+ sputtering at 50 μA	
	B.E.[a] (eV)	Peak height (cm)	B.E.[a] (eV)	Peak height (cm)
Cd				
$3d_{5/2}$	404.9 (405.0)	10.2	405.0	11.3
$3d_{3/2}$	411.7 (411.7)	7.0	411.7	8.1
4d			10.9 (11.0)	6.3
S				
$2p_{3/2}$	161.4 (161.3)	10.9	161.5	11.5
$2p_{1/2}$	162.0 (162.0)	9.4	162.0	10.3

[a] Binding energy. The binding energy values reported for Cd 3d, 4d and S 2p reported in [10–15] for CdS are given in parenthesis.

indicates that the photoreduction of Pd^{2+} is mediated by surface states. It is known that the Cd 4d level shifts to a lower binding energy whenever there is a formation of Schottky barrier between the metal and CdS in the case of metallized CdS [10]. A negative shift of 0.7 eV is observed in the case of an Au/CdS Schottky diode [10]. In the case of Pd/CdS there is no shift in the binding energy of the CdS 4d electrons (Table III), indicating that the contact between CdS and Pd is ohmic. We have earlier reported [3] that the photodeposited Pd on CdS serves as a good reduction centre. Furthermore, it is also known that for metals to function as reduction centres on n-type semiconductors such as CdS, the metals should form an ohmic contact with the semiconductor [16], as the formation of Schottky barrier would drive the electrons away from the metal. In the case of Pd/CdS the binding energy values of Cd 3d, 4d and S 2p (Table III) agree well with those reported for CdS [10–15], indicating that there is no charge transfer from Pd to CdS, and vice versa. That is, photodeposition of Pd does not affect the binding energy values of the Cd 3d, 4d and S 2p electrons. This is possible only if the contact between Pd and CdS is ohmic. There is no shift in the binding energy values of Cd 3d, 4d and S 2p electrons, showing the absence of compounds such as PdS, which could arise by the reaction of $PdCl_2$ with CdS. Hence, it is evident that Pd^{2+} is not reacting with CdS. It is known that photodeposition of metals on semiconductors normally results in the formation of ohmic contacts [17, 18]. In the present investigation, photodeposition of Pd on CdS also results in an ohmic contact.

Thus, the XPS studies indicate that the photodeposition of Pd on CdS is mediated by surface states and the photodeposited Pd is in the zero oxidation state; however, it is prone to aerial oxidation and the photodeposited Pd forms an ohmic contact with CdS.

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