

Interface and surface analysis of Ru/CdS

I. B. RUFUS*, V. RAMAKRISHNAN, B. VISWANATHAN, J. C. KURIAKOSE
 Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Metallized CdS serves as a better photoanode and photocatalyst than naked CdS [1-6]. As most of the noble metals exhibit low over voltage for hydrogen evolution, they serve as good proton reduction centres. So, noble metals are photodeposited or vacuum deposited (sputter coated or thermal evaporation) on CdS to produce metallized CdS. The interface and surface properties of metallized CdS depend on the method of metallization. Because the photoelectrochemical, as well as photocatalytic, behaviour of metallized CdS is greatly influenced by its interface and surface properties, the interface and surface characterization of metallized CdS becomes inevitable. Ru/CdS prepared by photodeposition of Ru serves as a better photoanode and photocatalyst than CdS. However, there is no detailed report on the interface and surface studies of Ru/CdS. As mentioned earlier, because the photoelectrochemical and photocatalytic properties of Ru/CdS depend on its interface and surface characteristics, one can get very useful information about the interface and surface of Ru/CdS from its photoelectrochemical and photocatalytic behaviour. Hence in the present investigation, in addition to the usual surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and diffuse reflectance spectroscopy (DRS), photoelectrochemical (PEC) and photocatalytic methods have also been effectively utilized to analyse the interface and surface of Ru/CdS.

Ru/CdS is prepared as explained in [7]. Details of XPS, SEM, DRS, PEC and photocatalytic measurements are reported elsewhere [7-10].

From Fig. 1 and Table I, it is evident that, in addition to Ru, different oxides of Ru, such as RuO₂, RuO, RuO_{0.5} and RuO_x (x < 1), are present on the surface of Ru/CdS. However, argon ion sputtering removes some of these oxide layers, as indicated by the decrease in the O 1s peak height (Fig. 2). Furthermore, the increase in peak heights of Cd 3d, 4d and S 2p XPS peaks on argon ion sputtering (Table II) also indicates the removal of oxide layers. From Fig. 1, it can be seen that argon ion sputtering removes RuO₂ (the Ru 3d_{3/2} peak for RuO₂ at 286.3 eV completely disappears, while the Ru 3d_{5/2} peak for RuO₂ at 282.5 eV reduces to a small hump after argon ion sputtering). However, the other oxides of Ru, like RuO, RuO_{0.5} and RuO_x (x < 1),

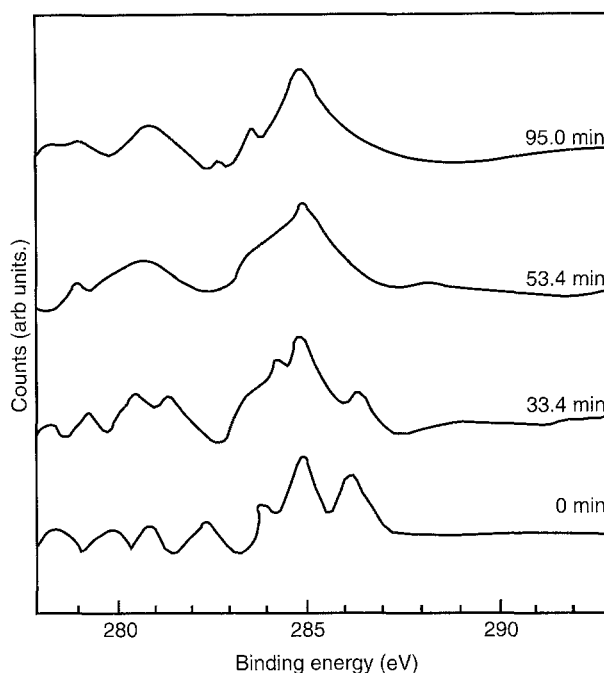


Figure 1 Ru 3d XPS peaks of Ru/CdS as a function of argon ion sputtering time.

TABLE I Various Ru species present on Ru/CdS

Energy levels of elements probed	Binding energy (eV)			Species assigned
	Observed	Reported	Reference	
Before argon ion sputtering				
Ru 3d _{5/2}	282.5	282.8	[11]	RuO ₂
O 1s	529.0	529.2	[12]	RuO ₂
Ru 3d _{5/2}	280.9	a		RuO
Ru 3d _{5/2}	Absent	281.6	[11]	RuCl ₃
O 1s	530.0	529.8	[12]	RuO
Ru 3d _{5/2}	279.9	b		RuO _x (x < 1)
Ru 3d _{3/2}	283.8	283.6	[13]	Ru
Ru 3d _{3/2}	286.3	c		RuO ₂
Ru 3d _{3/2}	284.9	d		RuO _{0.5}
After 95 min argon ion sputtering at 50 μA				
Ru 3d _{5/2}	279.0	279.1	[13]	Ru
Ru 3d _{3/2}	283.7	283.6	[13]	Ru
Ru 3d _{3/2}	284.8	d		RuO _{0.5}
Ru 3d _{5/2}	279.9	b		RuO _x (x < 1)
Ru 3d _{5/2}	282.7	282.8	[11]	RuO ₂
Ru 3d _{5/2}	280.9	a		RuO

^aA positive shift of 2.8 eV in binding energy indicates that Ru is in the +2 oxidation state.

^bLies between those reported for Ru and RuO, indicating the presence of RuO_x.

^cA positive shift of 3.3 eV implies that Ru is in the +4 oxidation state.

^dA positive shift of +1 eV in binding energy indicates that Ru is in the +1 oxidation state.

*Present address: Department of Polymer Science, University of Southern Mississippi, Box 10076, Hattiesburg, MS-39406-0076, USA.

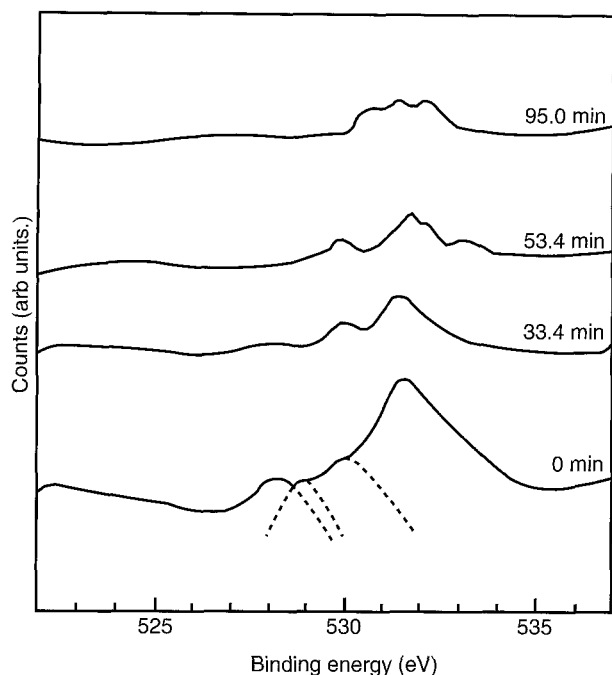


Figure 2 O 1s XPS peaks of Ru/CdS at different argon ion sputtering times.

could not be removed completely, even after 95 min of argon ion sputtering at $50 \mu\text{A}$. No RuCl_3 could be detected on the surface of Ru/CdS (Table I), indicating that no residual or unreacted RuCl_3 is left behind after the photodeposition of Ru from RuCl_3 , as Ru/CdS is thoroughly washed and dried. These observations show that Ru, as it is photodeposited, is in the zero oxidation state. But aerial oxidation of Ru, during the exposure of Ru/CdS to air (while drying), results in the formation of an oxide coating over Ru/CdS. Photodeposition of Ru on the illuminated face of CdS indicates that

photoreduction of Ru^{3+} is mediated by surface states [7, 8, 14]. In the case of Ru/CdS there is no negative shift in the binding energy of the Cd 4d electrons (Table II), indicating that the contact between CdS and Ru is ohmic [7, 8, 25]. The binding energy values of Cd 3d, 4d and S 2p (Table II) agree with those reported for CdS [15–20], implying that there is no charge transfer from Ru to CdS and vice versa. Further, it is known that photodeposition of metals on semiconductors normally result in the formation of ohmic contacts [21, 22]. In the present investigation, photodeposition of Ru on CdS also results in an ohmic contact.

PEC studies on Ru/CdS were carried out to probe the interface and surface of Ru/CdS further, as the photoelectrochemical characteristics are very sensitive to the interface and surface properties of the photoanode. The internal resistance of the PEC cell under illumination, $R_{\text{cell}(\text{photo})}$, increases only when the contact between the photoanode and the photodeposited metal is ohmic [9], and not otherwise [10]. Hence, an increase in $R_{\text{cell}(\text{photo})}$ of the PEC cell upon photodeposition of Ru on CdS photoanode (Table III) implies the formation of an ohmic contact between the photodeposited Ru and CdS. Photodeposition of Ru on CdS photoanode shifts the photocurrent onset potential to a more positive value (Table III) indicating the deposition of a neutral or positively charged species. However, XPS studies show that the photodeposited Ru is in a zero oxidation state. Table III also shows that the photocurrent at a bias of +1 V versus the saturated calomel electrode (SCE), which is mainly due to the photocorrosion of CdS [23, 24], decreases upon photodeposition of Ru on CdS; indicating that photodeposition of Ru on CdS decreases the

TABLE II X-ray photoelectron spectroscopic data on Ru/CdS

Energy levels of elements probed	Before Ar^+ sputtering		After 95 min Ar^+ sputtering	
	B.E. ^a (eV)	Peak height (mm)	B.E. ^a (eV)	Peak height (mm)
Cd				
3d _{5/2}	405.4	50.0	405.2(405.0)	91.0
3d _{3/2}	412.1	37.0	411.9(411.7)	68.0
4d	11.4	8.5	11.3(11.0)	13.0
S				
2p _{3/2}	161.8	9.3	161.8(161.3)	11.1
2p _{1/2}	162.0	6.9	162.0(162.0)	8.4

^aB.E., binding energy: values reported for Cd 3d, 4d and S 2p in [15–20] are given in parentheses.

TABLE III Effect of photodeposition of Ru on the photoelectrochemical characteristics of CdS (counter electrode), Pt-foil; reference electrode, SCE; electrolyte, 0.1 M KCl

Photoanode	Dark		$R_{\text{cell}(\text{dark})}^c$ V/I (k Ω)	Net photo		$R_{\text{cell}(\text{photo})}^d$ V/I (k Ω)	Photocurrent onset potential (V versus SCE)	Photocurrent at a bias of +1 V versus SCE (μA)
	V_{oc}^a (mV)	I_{sc}^b (mA)		V_{oc} (mV)	I_{sc} (mA)			
CdS	100	0.001	100	280	0.033	8.5	-0.65	245
Ru/CdS ($\theta = 0.38$) ^a	-16	-0.001	16	336	0.023	14.6	-0.46	210

^a V_{oc} open circuit voltage.

^b I_{sc} , short circuit current.

^c $R_{\text{cell}(\text{dark})}$, internal resistance of the PEC cell in the dark.

^d $R_{\text{cell}(\text{photo})}$, internal resistance of the PEC cell under illumination.

θ , fraction of surface of CdS covered Ru [23].

photocorrosion of CdS. Thus, it is clear that PEC methods could also be used effectively to study the surface and interface of metallized semiconductors, in addition to a conventional surface analysis technique like XPS.

Ultraviolet (u.v.) visible diffuse reflectance spectrophotometry (DRS) is another versatile surface analysis technique, that allows one to study the light absorption characteristics of semiconductors, and thereby their band gap excitation and relaxation processes. DRS studies (spectra not shown) reveal that the photodeposition of Ru extends the light absorption of CdS from about 575 to 625 nm, without affecting its band gap absorption (517 nm). This small increase in the tail end absorption of CdS, due to photodeposition of Ru, can be attributed to the excitation of a fraction of the valence band electrons of CdS to the energy levels arising out of the perturbation of the CdS lattice by Ru [25–27].

In order to have a better understanding of the interface of Ru/CdS, photocatalytic studies have been carried out. Photodeposition of Ru on CdS makes Ru/CdS a better photocatalyst than CdS (Table IV), as Ru serves as an efficient proton reduction centre. The contact between Ru and CdS should be ohmic for Ru to function as a reduction centre or sink for the electrons, as a Schottky barrier would drive the electrons away from Ru [28]. Thus, photocatalytic studies also support the formation of an ohmic contact between Ru and CdS.

Scanning electron micrographs of Ru/CdS (not shown) reveal that photodeposited Ru forms discontinuous layers on the surface of CdS. Photodeposition of metals on semiconductors usually results in the formation of ohmic contacts [21, 22]; further discontinuous metal layers are observed when the contact between the semiconductor and the photodeposited metal is ohmic [27]. Thus the formation of discontinuous layers by photodepositing Ru on CdS suggest the contact between them could be ohmic.

Photodeposited Ru on CdS is in the zero oxidation state. However, it is prone to aerial oxidation. Photodeposited Ru forms an ohmic contact with CdS. Photodeposition of Ru on CdS decreases its photocorrosion and increases its photocatalytic activity. Photodeposited Ru forms discontinuous metal layers on the surface of CdS. XPS, SEM,

DRS, photocatalytic and PEC methods serve as versatile tools in surface and interface characterization of metallized semiconductors.

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TABLE IV Photocatalytic hydrogen evolution from aqueous sulfide solution (reactant, 0.25 mol Na₂S aqueous solution (20 ml); pH, 13; weight of photocatalyst, 100 mg; temperature, 303 K)

Photocatalysts	Initial H ₂ evolution rate (μl h ⁻¹)
1. CdS	39
2. Ru/CdS (Ru 1.37 wt%)	242

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