Surface Analysis of Semiconductor-Incorporated Polymer Systems

2—Pt-Nafion and Pt-CdS-Nafion

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Pt-Nafion (chemically reduced and sputtered Pt) and Pt-CdS-Nafion membranes were studied by x-ray photoelectron spectroscopy. The chemically deposited Pt was completely reduced to Pt^0 and was more concentrated in the surface region than in the interior. The sputtered Pt (100 Å thick) was distributed within the first several hundred Ångstroms of the Nafion, probably involving Pt migration into it, during the RF sputtering process. Changes of the $Pt(4f_{7/2})$ linewidth indicate interactions between CdS and Pt. The relatively high activity of the 100 Å sputtered Pt-CdS-Nafion membrane for the photoassisted production of H_2 in aqueous 0.1 M S^{2-} solution is discussed.

INTRODUCTION

In a previous paper[1] we reported on the photodriven hydrogen formation from water using Nafion films containing semiconductor particles. The Pt-CdS-Nafion system showed several interesting properties: (a) cubic CdS is more active than hexagonal CdS, (b) the efficiency of hydrogen production is comparable to colloidal systems, (c) the photoactivity of a used membrane system can be restored by washing with boiling water.

Active semiconductor incorporated polymer systems have also been reported by other investigators.[2-5] These polymer membrane systems have potential for product separation in integrated systems.[6,7] Thus, it is important to characterize the interfaces between the polymer, the semiconductor and the metal.[8]

Recently, we also reported on the characterization of Nafion and CdS-Nafion films by x-ray photoelectron spectroscopy (XPS).[9] There were several important observations: (a) the number of surface cation exchange sites in Nafion is small, (b) the CdS concentration at the surface of the cubic CdS-Nafion is 140 times higher than that of the hexagonal CdS-Nafion, and (c) the grey-blue deposit formed on the surface of cubic CdS films during irradiation is atomic sulfur.

In this paper we report on the XPS characterization of Pt-Nafion (chemically reduced and sputter deposited) and Pt-CdS-Nafion films.

EXPERIMENTAL

Nafion (Du Pont 117, 0.018 cm thick) perfluorinated cation exchange membranes were used and prior to incorporation of Pt and/or CdS these films were cleaned as described elsewhere.[1] The platinized Nafion films were prepared by two methods as follows.

Method I

The chemical deposition of Pt was carried out by soaking Nafion films (1 cm × 1 cm) in a dilute solution of $Pt(NH_3)_4Cl_2$.[10] The amount incorporated depended on the soaking time and was determined by optical absorption spectroscopy. After incorporating the complex, the films were immersed in a 0.1 M $NaBH_4$ solution to reduce the Pt^{2+} to Pt^0 (creating black films). The resulting films were washed repeatedly with boiling distilled water until the water was neutral. The amount of Pt incorporated was between 0.02 and 0.06 mg cm^{-2}.

Method II

Pt was coated onto Nafion films by RF Ar^+ sputtering (2×10^{-2} torr flowing Ar, 99.999% purity) with a standard RF thin film sputtering module. The base pressure was 2.0×10^{-6} torr. The Nafion films were placed on a water-cooled substrate plate for deposition. The rate of deposition was approximately 10 Å s^{-1} (measured by optical absorption of Pt deposited on a glass slide).

The photogeneration of hydrogen was carried out using 0.1 M Na_2S solution and a 1 kW xenon lamp. The details are described in previous paper.[1]

The crystallite sizes of Pt were estimated from x-ray diffraction (XRD) line widths. Scanning electron microscopy (SEM) was done with a JEOL JSM-35C system. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Vacuum Generators ESCALAB system with Mg Kα radiation. The core level binding energies (BE) were all referenced to the surface hydrocarbon contamination C 1s peak (284.5 ev), which was easily distinguished from Nafion carbon.

RESULTS AND DISCUSSION

Pt-Nafion

Chemically deposited Pt. By XRD line broadening, the Pt crystallite size in these films is ca. 100 Å. XPS of both the fresh and reduced platinized Nafion films gives F 1s, C 1s and O 1s peaks at BEs of 688.9, 291.3 and 531.9 eV, respectively. These are consistent with other work with *fresh* Nafion films containing no Pt.[9] With the Pt complex

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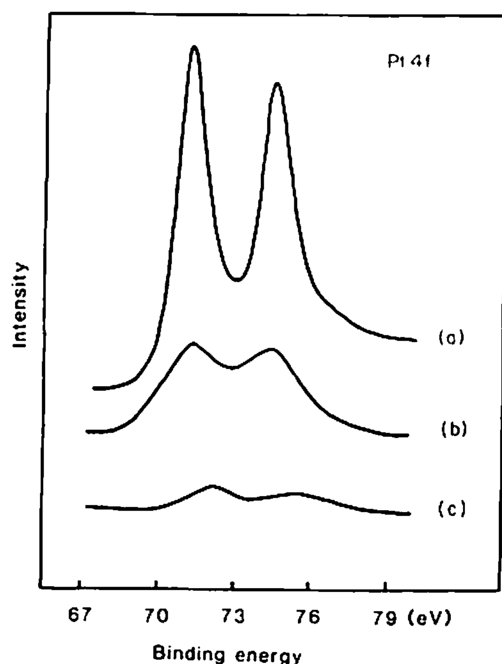

Figure 1. Pt 4f XPS spectra: (a) Pt foil; (b) Pt-Nafion (chemically reduced Pt); (c) Pt complex-Nafion.

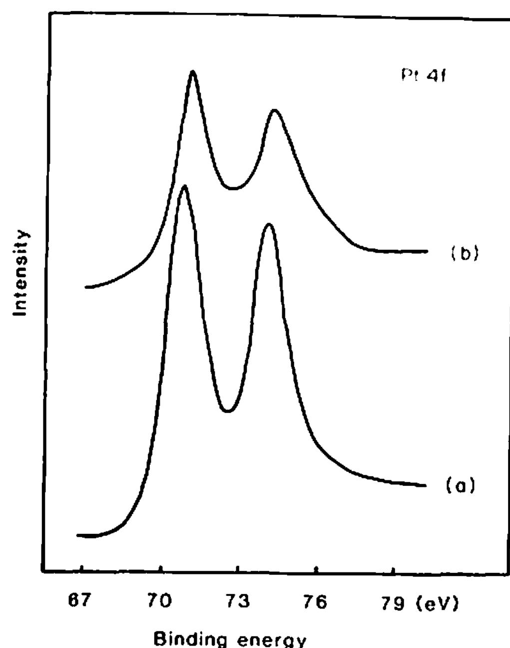

Figure 3. Pt 4f XPS spectra of Pt-Nafion (sputter deposited Pt) film before (a) and after (b) Ar bombardment.

incorporated but not reduced, the Pt $4f_{7/2}$ *BE* is at 72.0 eV (Fig. 1). After reduction with $NaBH_4$, it shifts to 71.1 eV. For a Pt foil, the measured *BE* is 71.2 eV (Fig. 1), indicating that Pt complexes lying within the XPS sampling depth are completely reduced to Pt and that the Pt particles are large enough to give the bulk Pt *BE*s.

The surface atomic ratio Pt 4f/F 1s after reduction is 45 times higher than that before reduction. This implies that during reduction, Pt tends to move to the surface from interior cation exchange sites. A similar phenomenon occurs during CdS formation from incorporated Cd^{2+}.[9]

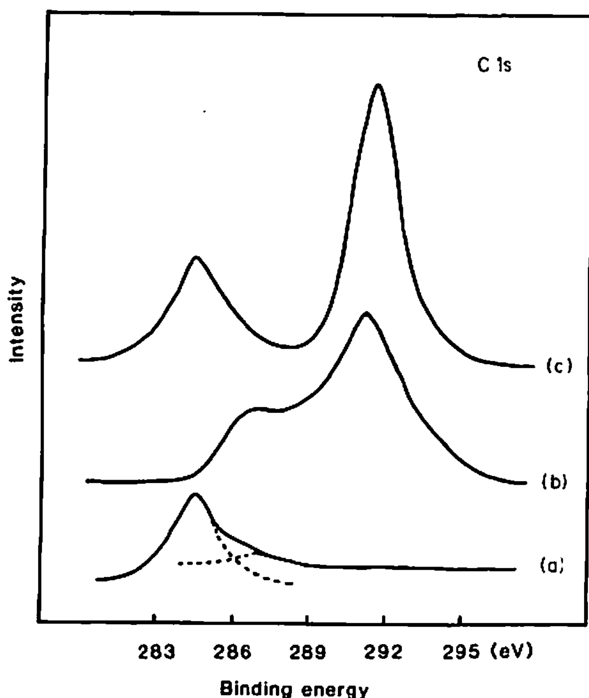

Figure 2. C 1s XPS spectra of Pt-Nafion (sputter deposited Pt) film before (a) and after (b) Ar bombardment; (c) fresh Nafion film (no Pt).

Sputtered Pt. The surface characterization focused on 100 Å Pt films since they give the highest hydrogen generation activity.[1] The 100 Å Pt film surface was glossy and transparent. The XRD showed no peaks and SEM could not detect any Pt particles. These two observations indicate that the Pt films are non-crystalline.

The *BE* of F 1s is the same as that of a fresh Nafion film. Before sputtering, Figure 2 shows a C 1s peak at 287.5 eV in addition to the residual hydrocarbon peak at 284.5 eV. There was no C 1s signal at 291.3 eV from Nafion itself. The Pt $4f_{7/2}$ *BE* is 70.8 eV (Fig. 3), very close to that of Pt foil (Fig. 1).

After Ar^+ bombardment (9 kV, 70 μA) for 2 min, the Pt $4f_{7/2}$ *BE* shifts to 72.6 eV from 70.8 eV (Fig. 3). The surface atmic ratio (Pt/F) decreased from 26.0 to 0.04, suggesting that most of the Pt film has been sputtered and only highly dispersed Pt remains. The C 1s region shows peaks at 287.5 and 291.3 eV. The intensity of the low *BE* (287.5 eV) peak increases with Ar^+ bombardment.

The high *BE* peak (291.3 eV) is assigned to Nafion carbon. The Pt $4f_{7/2}$ peak at 72.6 eV and the C 1s peak at 287.5 eV can be explained in terms of highly dispersed Pt surrounded by carbon atoms derived from the Nafion film. A similar phenomenon has been observed for highly dispersed metals and at support-metal interfaces and is dominated by final state relaxation effects.[11,12]

We estimate that the sputtering of Pt is 220 Å min^{-1} (2 kV, 100 μA)[13] and calculate that Pt extends approximately 1500 Å below the surface of the Nafion film. While this calculation is, at best, semiquantitative because of unknown differential sputtering effects, there is clearly significant penetration of Pt into the Nafion.

Table 1. Resistivity of Pt coating on glass slide and Nafion

Pt thickness	Resistance	
	Glass slide	Nafion (117)
0		8 MΩ
100 Å	2 KΩ	70 KΩ
ca 1000 Å	60 Ω	120 Ω

The x-ray fluorescence of a cross-sectioned film was measured, but the concentration of Pt was too small to detect.

We measured the lateral resistance (Table 1) of the Pt coating on glass slides and on Nafion by attaching two electrical leads to the films. As seen in Table 1 the 100 Å Pt film on Nafion is about 35 times less conductive than the corresponding glass slide, but the 1000 Å thick Pt films have similar conductivity. The results are consistent with discontinuous, rougher and more penetrating Pt films on Nafion than on the glass surface. We have no information about the size and structure of the particles making up this discontinuous film. However, the porous and relatively soft Nafion probably allows the observed penetration of Pt.

Na_2S effect. Both types of platinized Nafion films were soaked in Na_2S (0.1 M) solution for three hours, dried, and analyzed by XPS. The S 2p peaks (Fig. 4) of chemically and sputter deposited Pt show the *BE*s at 169.0 eV (oxidized sulfur) and 162.1 eV (sulfide), respectively. Treatment of the Pt-free Nafion with Na_2S gives an oxidized sulfur XPS peak like the chemically deposited Pt film. This suggests that the latter surface is dominated by Nafion. On the other hand, sulfide is stable on the sputter deposited Pt surface and the sulfur concentration within the XPS sampling zone is 150 times that of the chemically deposited Pt (XPS peak intensities). The formation of sulfide caused no *BE* shift of the Pt $4f_{7/2}$ peak, but the linewidth increased from 1.8 to 2.9 eV, suggesting that the sulfide species does interact with Pt.

Pt-CdS-Nafion

Films containing cubic, rather than hexagonal, crystallites of CdS were used for these experiments because of their high activity for hydrogen generation when platinized.[1]

Chemically deposited Pt/CdS. In these films, chemically deposited Pt was prepared prior to cubic CdS incorporation. The *BE*s of Cd 3d, S 2p, C 1s and F 1s are equal to those of the cubic-CdS films. The Pt $4f_{7/2}$ *BE* is 72.1 eV (oxidized Pt). After irradiation in the presence of Na_2S solution, the *BE* dropped to 71.3 eV but the peak intensity did not change. Since prior to adding CdS the incorporated Pt complexes were completely reduced to Pt^0 (see above), the oxidized Pt must be formed during the cubic CdS incorporation process. To investigate this further platinized Nafion film was treated with boiling nitric acid and H_2S (i.e., the conditions for cubic CdS incorporation into Nafion film) in the absence of Cd^{2+}. The film became clear, the *BE* of Pt $4f_{7/2}$ shifted to 72.0 eV which is typical of oxidized Pt, and the peak intensity decreased. Retreating with $NaBH_4$ restored the

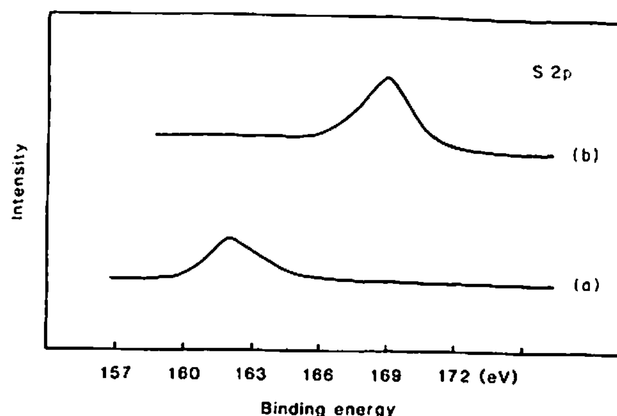

Figure 4. S 2p XPS spectra of Pt-Nafion soaked in Na_2S: (a) sputter deposited Pt film, (b) chemically deposited Pt film.

black color and the lower *BE* for Pt $4f_{7/2}$. These results confirm that the oxidized Pt species is formed under the conditions of the CdS incorporation.

Sputtered Pt/CdS. The 100 Å film of Pt was deposited by RF sputtering after cubic-CdS impregnation. The *BE*s of Pt $4f_{7/2}$, Cd 3d, C 1s and F 1s are similar to those of cubic-CdS-Nafion and Pt-Nafion films. Shifts of the Pt *BE* were not observed with irradiation. The linewidth of Pt $4f_{7/2}$ peak increased from 1.8 eV to 2.6 eV when CdS was incorporated, and can be understood in terms of changes in the Pt dispersion and/or longer lifetime of Pt core holes in the presence of CdS. Both reflect interactions between Pt and CdS.

The effects of adsorbed SO_3^{2-} and SO_4^{2-} species were also investigated. The films were soaked for 5 min in 0.1 M Na_2SO_4 solutions. After drying at room temperature, XPS spectra were measured. The S 2p *BE*s of the adsorbed SO_3^{2-} and SO_4^{2-} species are 167.5 and 168.1 eV, respectively. The S 2p *BE* of 168.1 eV is in agreement with the other reports[13] for sulfate but the *BE* of 167.5 eV for the adsorbed sulfite is slightly higher than the reported values (166.1-166.7 eV)[14-17] and probably indicates that some of the adsorbed SO_3^{2-} ions are oxidized to SO_4^{2-} species when the films are contacted with air. The S 2p peak, intensity for the SO_3^{2-} soaked film is ca. 6 times higher than that with SO_4^{2-}.

When Na_2SO_3 solution was used as a sacrificial solution, the photoactivity for H_2 generation was poor.[18] One explanation is that strongly adsorbed species (SO_3^{2-} and/or SO_4^{2-}) on the surface inhibit the adsorption of H^+ and thereby retard the rate of electron capture to form hydrogen. Another possibility is that the larger size of SO_4^{2-} and SO_3^{2-} compared to S^{2-} retards migration into the Nafion films. In any case, it is clear that these ions are strongly adsorbed and are not good sacrificial electron donors.

Parenthetically we note that the hydrogen generation activity of these 100 Å Pt film systems was approximately $\frac{1}{3}$ that of chemically deposited Pt-CdS films.[1] This could be due to one or more of a number of reasons connected to the morphology and chemical state of the system. We also note that the photoactivity of a used film could be restored by washing with boiling water whereas the activity of a chemically reduced Pt film was restored by washing with water at 25 °C. Presumably, both types of Pt systems accumulate sulfur during irradiation.[1,9] We

have no insight as to why the boiling water treatment is necessary to recover the activity.

Photoactivity of both films. As noted above, the optimal hydrogen formation activity for the sputter coated Pt film is approximately ⅓ that of the chemically deposited Pt film. Since light will penetrate at least a few microns into the CdS and close proximity of Pt and CdS are required for good hydrogen generation activity, it is interesting to consider the high photoactivity of the sputter coated Pt film.

Upon formation of CdS, the XPS data[9] clearly indicates that CdS becomes more concentrated at the surface. Assuming a homogeneous Cd concentration in the near-surface region of the Nafion before (d_1) and after (d_2) CdS formation and assuming the surface atomic Cd ratio can be calculated from XPS (Cd/F) ratios, we find $d_1/d_2 = 7.14 \times 10^{-3}$. This ratio indicates that most of the Cd lies within the XPS sampling depth after CdS is formed. While x-ray fluorescence of a cross-sectioned film shows Cd throughout the Nafion, there is a definite increase in concentration near the surfaces[9] that is consistent with these results. Thus, the calculation presented here shows qualitatively that most of the electron-hole pairs, generated by light absorption in CdS, are formed within less than a few hundred Angstroms of a Pt site. Consequently, it is not surprising that the chemically-reduced and sputter-deposited Pt films have activities of the same order of magnitude.

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