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52. Photoelectron Spectroscopic Determination of the Structure of Thin Platinum Silicide Layers Formed on Si(100) and Si(111) for Use as Electrodes

G. A. Hope, F.-R. F. Fan, and A. J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

ABSTRACT

Platinum silicide was grown on (100) and (111) silicon by vacuum annealing an evaporated layer (0-15 nm thick) at 400°C, immediately following deposition. The element distribution in the product layer was measured using electron spectroscopy (XPS and AES) in conjunction with argon ion sputtering of the sample. The silicide thus produced was covered by a thin surface layer of SiO_2. The decrease in platinum concentration with increasing penetration into the sample was characteristic of a reaction mechanism in which a platinum species diffuses into the Si.

Among the methods for protecting the surface of n-type silicon from photocorrosion when employed as an electrode for generating highly oxidizing species, such as chlorine and oxygen in photoelectrochemical (PEC) cells, the use of thin noble metal silicide films has been particularly beneficial (1, 2). Such films, sometimes suitably modified with metal oxides or other catalysts, can also promote the interfacial electron transfer reactions of photogenerated carriers. Moreover, several silicide systems have been investigated because of their application in the electronics industry (3). The silicides formed from Pd(4), Pt(5), and Ni(6) have been particularly well studied. There is, however, only limited information available on the structure and properties of the very thin layers (<50 nm) which are of primary interest in electrochemical studies. In this paper, we report the results of x-ray photoelectron spectroscopy (XPS or ESCA) and Auger electron spectroscopy (AES) studies of the Pt-Si films formed on single crystal surfaces of Si.

* Electrochemical Society Active Member.

Experimental

Substrates for silicide growth were n-Si(100) and p-Si(111) (0.4-0.6 Ω cm) donated by Texas Instruments. The crystals were polished with 0.6 μm alumina and etched with HNO_3:HF:HOAc (3:3:1) containing 0.03% Br_2 for 10-15 sec, followed by concentrated HF for 10-15 sec, and then washed with distilled water and methanol immediately prior to insertion into the evaporation chamber. A known mass of platinum (Alfa Ventron, 99.9%) was evaporated from a tungsten filament in an Edwards E306A vacuum coating system. The source to substrate distance was 8 cm and base pressure during evaporation did not exceed 1×10^{-6} Torr. The silicon crystals were supported by a mica plate resting on a molybdenum heating stage. Following Pt deposition, the temperature of the heating stage was raised to 400°C and held to within ±10° for a few minutes up to 1 hr. The temperature was measured with a chromel-alumel thermocouple in contact with the mica. After heat-treatment, the samples were allowed to cool and removed from the vacuum system for study by XPS, AES, and scanning electron microscopy. XPS measurements were made of the Pt 4f, Si 2p, and O 1s peaks with a Physical Electronics 548 instrument using a Mg Kα source (2 mm spot diam) on the as-prepared sample surface and following varying periods of 5 keV argon ion bombardment at a current density of 6 μA-cm^{-2}. The AES data were obtained on a Physical Electronics 590 system, the exciting radiation being 5 keV electrons with a sample current of 240 μA over a spot diameter of 3 μm. The sample spectra were measured from 25 to 2000 eV for the as-prepared specimens and between sputtering periods. During sputtering (at 40 μA-cm^{-2} with 3 keV argon ions, rastered over 6 mm^2) the intensities of the Si KL_2L_2 C KL_2L_2 O KL_2L_2 and Pt $N_5N_7O_4$ peaks were monitored. The sample topography was investigated with a JEOL JSM 35C electron microprobe analyzer (EMP).

Results and Discussion

When the cleaned unannealed silicon surface was inspected in the EMP, it was found to be smooth and slightly pitted, the pits having been generated in the cleaning process. Reaction of this surface with platinum to form the silicide altered the topography only slightly, generating no detectable surface structure at magnifications up to 100,000 times. Reacted samples were also investigated by scanning mode AES, where the surfaces resembled those observed in the EMP. AES spectra of the surface both before sputtering and after having been sputtered until approximately 9 nm of the sample had been removed are shown in Fig. 1. The unsputtered surface was contaminated with carbon and oxygen and, although the Si peak at 92 eV was small, it had a shape that resembled that found for SiO_2. There were only very weak peaks which could be attributed to Pt. The sample spectrum after sputtering contained only small signals for carbon and oxygen, the major peaks were those of silicon and platinum. On further sputtering of the sample, the platinum peaks decreased in intensity and eventually only the silicon signals were obtained.

Samples were also depth-profiled while monitoring the Si KL_2L_2, C KL_2L_2, O KL_2L_2, and Pt $N_5N_7O_4$ Auger peaks to determine the elemental distribution. A typical depth profile is presented in Fig. 2. The original surface of the sample was characterized by a region approximately 5 nm thick, which was enriched in oxygen and carbon and deficient in platinum. Beneath this surface region the maximum platinum signal was obtained and, as sputtering removed more of the sample, the platinum signal decreased and the silicon signal increased. This was observed for samples with annealing times as short as 5 min at this temperature. The intensity of the Si peak reached a maximum when approximately 21 nm had been sputtered from the surface; however, the

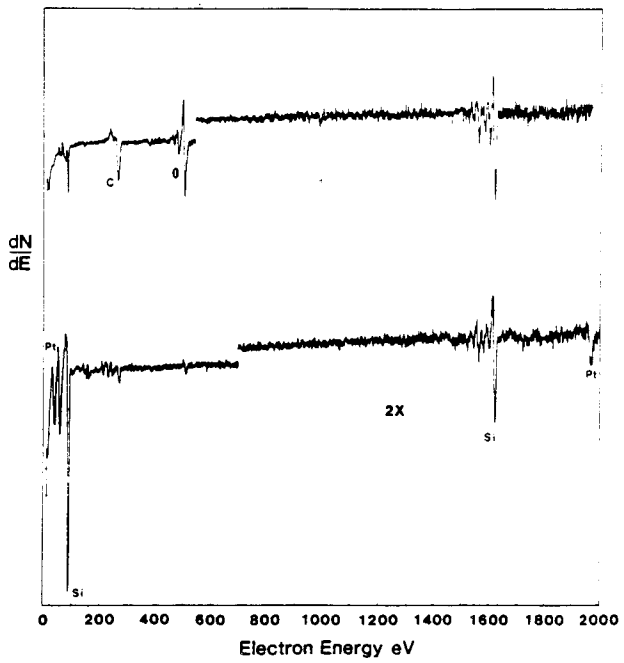

Fig. 1. The Auger electron spectrum of a platinum silicide sample prepared by annealing an evaporated Pt film on (100) n-Si at 400°C for 30 min. For the upper spectrum, the sample had not been sputtered, and the lower spectrum was taken after approximately 9 nm of the sample had been removed.

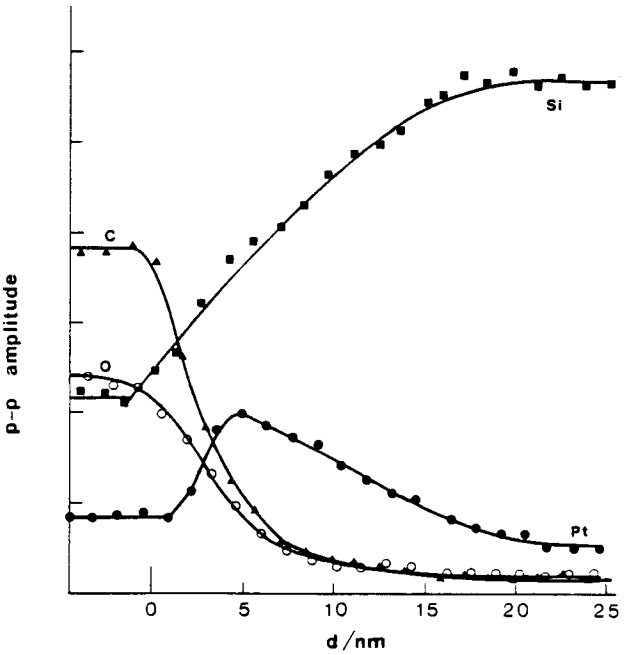

Fig. 2. The elemental depth profile of the sample of Fig. 1. This profile shape is typical of all annealed samples.

platinum signal was still present and continued to decrease with sputtering—it was present even after 30 nm of sample had been removed.

The information provided by depth-profiling the silicide layer and monitoring the surface composition with AES gives strong support for a model of silicide formation in which platinum is the mobile species, since it is the platinum which penetrates the silicon. This mechanism is in agreement with that proposed from tracer studies using ^{31}Si (7), but contrary to that proposed on the basis of Rutherford backscattering (RBS) using thicker silicide layers (8, 9). It is possible that the sputtering of the silicide does not remove the platinum

fully; however, Poate *et al* (10), have studied the sputtering process in the argon ion energy range which we have used and found almost stoichiometric sputtering of PtSi. For the pure materials, Pt sputters 2.4 times as fast as Si. Additional information on the chemical nature of the silicide layer and the extent of platinum penetration into the silicon was obtained with high resolution XPS. In Fig. 3, the changes in the silicon 2p peak are shown for various depths of sample sputtering. The initial peak is significantly broadened and consists of a higher energy component, located where the Si 2p peak in SiO_2 is found as well as a sharper peak closer to the elemental Si peak location. The Si 2p peak narrows, shifts to lower energy, and increases in strength after approximately 2 nm of sample had been sputtered away; this result indicates that the thin surface layer of SiO_2 present on the sample was removed. The energy of the silicide Si 2p peak was 99.3 ± 0.3 eV determined by reference to the silicon substrate after the Pt $4f_{7/2}$ signal was no longer detected. O 1s peak intensities were only significant in the initial 3 nm of the sample. The Pt 4f peaks were also measured after each sputtering, and the energy of the Pt $4f_{7/2}$ peak was measured relative to Pt $4f_{7/2}$ peak obtained from a platinum foil mounted next to the silicon. Typical scans of the Pt 4f peaks for varying degrees of sputtering are shown in Fig. 4. The energy of the silicide Pt $4f_{7/2}$ peak is approximately 1.6 eV higher in energy than for the metal, Pt° has a value of 72.5 ± 0.2 eV. This is most probably the value for PtSi which must be intergrown with silicon. Note that atomic ratios of Pt/Si > 1, with a stoichiometry of PtSi near the electrode surface, have also been found (2); the composition of the surface layer depends upon the amount of Pt deposited and the annealing time. From the intensity data obtained with the XPS measurements, a depth profile can be drawn, derived from the stronger platinum signal, and obtained using higher energy argon ions operated at a lower ion current density to give a slower sputtering rate than that used to obtain the AES profile. The XPS derived Pt-Si depth profile is presented in Fig. 5. This profile resembles the AES depth profile in elemental distribution, and provides additional information on the composition of the platinum containing layer.

Several important conclusions can be drawn from the depth profiles and the AES and XPS spectra. First, the depth resolution obtained with XPS and AES show

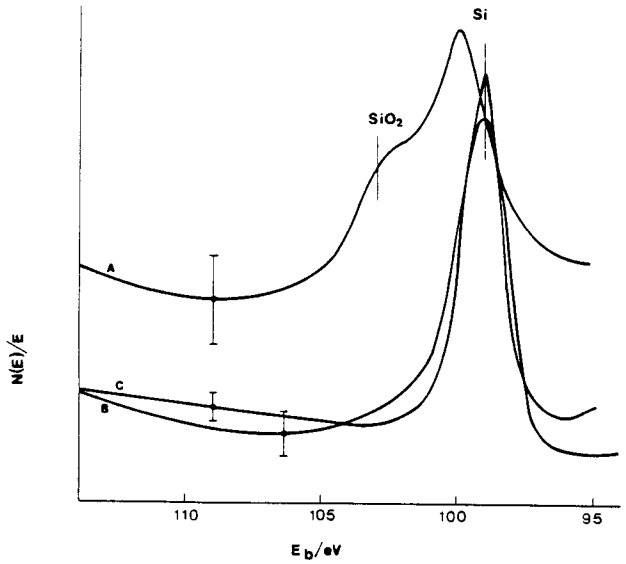

Fig. 3. Variation in the Si 2p peak shape with extent of sputtering (A) lightly (1 nm) sputtered with Si 2p peak shape characteristic of the presence of SiO_2, (B) Si 2p peak after approximately 5 nm of the sample have been removed, (C) after 15 nm removed.

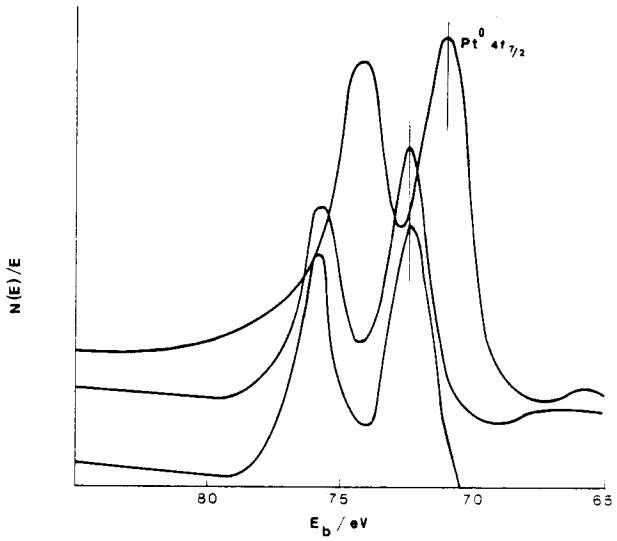

Fig. 4. The Pt 4f peak shape and location in the silicide layer compared to a platinum foil standard (upper curve) (A). The spectra were recorded after 10 (B) and 18 (C) nm (lower curve) were sputtered away.

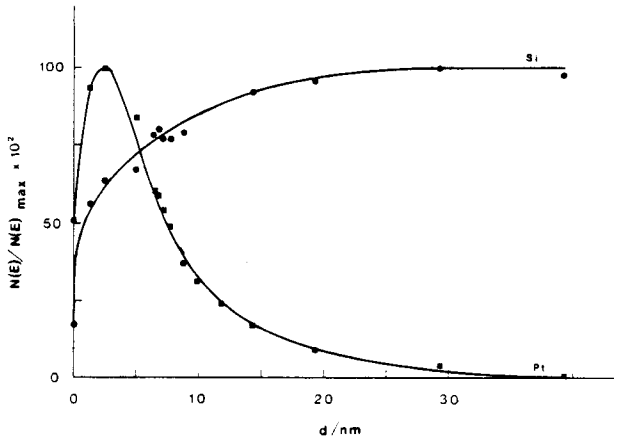

Fig. 5. The XPS depth profile showing the variation in element peak intensity as a function of sputtering depth.

that the thin Pt° films are converted into silicide containing layers which are approximately 4 times thicker than the original metal film. This layer does not achieve a uniform PtSi stoichiometry, and under the conditions here was richer in silicon, supporting a model which involves diffusion of platinum into the silicon substrate. Under these conditions of preparation, there was also no discrete PtSi/Si interface, and the only oxygen or carbon contamination is located close to the sample/vacuum interface. The XPS result presented in Fig. 3 shows that SiO_2 is present at the vacuum/sample surface, although some oxygen is detected at greater depths into the sample using AES. Since these signals are also associated with carbon, the source of the oxygen is probably related to oxidation of Si, prior to platinum film deposition. There is no evidence to support the intergrowth of Pt-Si and SiO_2 throughout the film. The diffuse nature of the silicide layer on silicon probably strongly influences the properties of any Schottky barrier between this layer and the silicon substrate.

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