Raman spectroscopy of PtSi formation at the Pt/Si(100) interface

J. C. Tsang, Y. Yokota, R. Matz, and G. Rubloff
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 12 September 1983; accepted for publication 22 November 1983)

We demonstrate the use of Raman spectroscopy with a multichannel detector to characterize the growth of PtSi on Si(100). The vibrational modes of surface silicide layers as thin as 10 Å and PtSi layers less than 40 Å thick buried under 140 Å of Pt have been observed without the need for any special sample geometry for signal enhancement. The Raman spectra can identify the silicide layer, estimate its thickness, and demonstrate its crystalline quality. This can be done on an arbitrary substrate, in air and without any special sample preparation.

PACS numbers: 78.30.Er, 68.30.+z, 68.55.+b, 68.48.+f

A description of the structure and bonding of the metallic layer at the interface is necessary for an understanding of the properties of a metal-semiconductor system. The experimental characterization of such an interfacial layer is difficult since it is often thin and buried under a much thicker layer of unreacted metal. In this letter, we use multichannel Raman spectroscopy to quantitatively characterize the formation of PtSi at the interface with Si(100). Raman spectra from PtSi layers as thin as 10 Å and from 40 Å of PtSi under 140 Å of Pt have been observed. We use the Raman spectra to identify the PtSi layer, estimate its thickness, and describe its crystallographic order. Our samples were reacted on crystalline Si under highly controlled conditions. They were independently characterized by surface electron spectroscopy, Rutherford backscattering, and transmission electron microscopy. Our ability to work on single crystals means we avoid the previous requirement of a unique sample geometry producing an external enhancement of the electromagnetic fields. Therefore, with its ability to probe more than 100 Å below a surface to observe a buried layer, Raman scattering can be a powerful tool in the characterization of silicides and interfaces.

The observation of Raman scattering from 10-Å-thick PtSi requires (1) a sensitive detector and (2) a substrate and overlayer (if the silicide is buried) producing little emission in the spectral range of interest. We use a multichannel Raman scattering system. The rejection and analysis of the elastically and inelastically scattered light is done by a subtractive dispersion double monochromator followed by a spectrograph. The scattered light is detected by a cooled SiT vidicon. This system has been used to detect Raman scattering from molecular monolayers adsorbed on metallic films. The Raman spectra were excited with 100 mW of light at wavelengths between 6471 and 4579 Å. Measurements of 521-cm⁻¹ zone center TO phonon of Si as a function of excitation power show heating due to the laser is less than 50 K at 300 K. The measurements were made at 300 K under flowing He to reduce the intensity of Raman scattering from the atmosphere.

Previous studies by Nemanich et al. on 2000-Å thick PtSi films show optic phonons between 80 and 200 cm⁻¹. This is a propitious region for crystalline Si since second order scattering occurs above 200 cm⁻¹ and defect induced scattering is weak. Contrast, in α-Si, disorder induced Raman scattering below 200 cm⁻¹ can obscure the silicide signal. Since Pt has the bcc structure, there are no Pt optic phonons to contribute to normal first order Raman scattering.

Our samples were prepared in an ultrahigh vacuum (UHV) system with a base pressure of 5 × 10⁻¹¹ Torr. Si wa-
fers were etched in HF, washed in ethanol, introduced into the UHV chamber, annealed, Ar⁺ sputter etched, and then annealed again at 1000 °C. The atomically clean Si(100) surfaces showed a well defined c(4 × 2) reconstruction. Pt was deposited on the Si by sublimation from a Pt filament. Deposition rates were about 0.1–0.5 Å/min and the thickness monitored by a quartz crystal microbalance. The samples were reacted in situ. The results of Auger and photoemission spectroscopy and transmission electron microscopy (TEM) studies of these samples are discussed separately. The Raman measurements were made after the samples were removed from UHV. Some samples were annealed in flowing He after removal from the UHV chamber.

Figure 1 shows the Raman spectrum of PtSi for different Pt thicknesses. Figure 1(a) is the Raman spectrum of Si. The structure between 220 and 350 cm⁻¹ is due to two-photon scattering. The weak structure at 150 cm⁻¹ has been attributed to defect induced scattering while the sharp lines between 50 and 120 cm⁻¹ are due to atmospheric scattering. The PtSi spectra shown in Figs. 1(b)–1(d) were obtained on samples annealed for 30 min at 500 °C. TEM of these samples shows only the presence of PtSi with no other phases (e.g., Pt, Si, pure Pt) detected. Figure 1(b) is the Raman spectrum from the reaction of 5 Å of Pt on Si(100). There is a shoulder superimposed on the edge of the elastic scattering background at about 85 cm⁻¹ and a well defined line at 140 cm⁻¹. These structures are the same as those seen in Fig. 1(c), the Raman spectrum of PtSi from 15 Å of Pt on Si(100) after 500 °C annealing. There are sharp lines at 82 and 140 cm⁻¹ with weaker structures at 150 and 260 cm⁻¹. Figure 1(d) is the Raman spectrum from Si(100) reacted with 160 Å of Pt, optically, essentially bulk PtSi. These phonon energies are identical to those obtained by Nemanich et al. for PtSi although the relative intensities of various lines differ. The strength of the 82 cm⁻¹ mode could mask a weak signal at 88 cm⁻¹ from a small amount of Pt, if present. The similarities of the Raman spectra in curves (b)–(d) demonstrate that Raman scattering can be used to identify PtSi as thin as 10 Å.

The second order Raman scattering from the Si substrate provides a means to normalize the intensity of the Raman scattering from the Si substrate.

Figure 2 shows the evolution of the Raman spectrum of PtSi on Si(100) by reaction at the Pt/Si(100) interface. Figure 2(a) is obtained from the deposition of 15 Å of Pt at room temperature. Surface electron spectroscopy shows silicide-like chemical bonds are formed within the first 10–20 Å of Pt deposition. The Raman spectrum shows broadened features near 80 and 150 cm⁻¹ indicative of these silicidate bonds. Figures 2(b)–2(e) show the growth of PtSi by thermally induced contact reaction of a thicker, unreacted Pt metal
overlayer. Figure 2(b) is the spectrum obtained from the deposition of 160 Å of Pt on Si without annealing. The scattering from the Si substrate and the PtSi interface is greatly reduced by the attenuation of the unreacted Pt. There is little evidence in Fig. 2(b) for the initially formed silicide layer seen in Fig. 2(a). This stems from the poor signal to noise ratio and the discontinuous morphology of the 15-Å Pt film which is discussed by Matz et al.5 The Raman spectra obtained from 160 Å of Pt on Si(100) after 30 and 480-min anneals in He at 230°C are shown in Figs. 2(c) and 2(d), respectively. We observe the emergence of structure at 82 and 140 cm⁻¹ in these spectra.

Annealing for 30 min at 300°C produces a silicide Raman spectrum [Fig. 2(e)] at least 20× stronger than the spectrum in Fig. 2(d). While TEM observes the PtSi phase only on the 300°C-annealed sample, it barely resolves the reacted silicide layer in the sample used for Fig. 2(d); we estimate the silicide thickness is between 20 and 60 Å, which is consistent with the relative intensities of Figs. 2(d) and 2(e). The linewidths of the fully reacted PtSi are less than 6 cm⁻¹. In contrast, the initial room temperature reaction shows broad Raman lines with a width greater than 20 cm⁻¹. The former widths are characteristic of well ordered, crystallized materials while the latter are characteristic of materials where there is short range, local order, but no long range order.12 The appearance of sharp lines in Fig. 2(d) suggests the silicide growing from the Pt-Si interface in the 160-Å Pt samples has long range order, even when it is only 20–60 Å thick.

A well defined Pt₅Si phase is not observed on our samples in TEM and surface spectroscopy or these Raman measurements under the deposition and growth/reaction conditions of our UHV preparation. This is discussed more fully elsewhere.8

In conclusion, we have shown that Raman scattering can (1) detect silicide layers as thin as 10 Å on single crystal silicon and (2) detect silicide layers as thin as 20–60 Å even when covered by > 100 Å of Pt. The Raman spectrum may be used to identify silicide formation and the likely silicide phase as well. The widths of the Raman lines can provide information about the long and short range order present in the silicide. While this information can be obtained by other probes, Raman scattering can be applied in a nonvacuum environment, with a surface that is not atomically clean and nondestructively (i.e., without having to etch away the Si substrate as required for TEM).

This work was partially supported by the Office of Naval Research.

---

Minority-carrier injection annealing of electron irradiation-induced defects in InP solar cells

M. Yamaguchi, K. Ando, A. Yamamoto, and C. Uemura
Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki-ken 319-11, Japan

(Received 10 October 1983; accepted for publication 2 December 1983)

The first observation of minority-carrier injection annealing of radiation-induced defects in InP is reported. Minority-carrier injection due to both forward bias application and light illumination at room temperature after electron irradiation is shown to enhance defect annealing in p-InP and to result in the recovery of InP solar cell properties. These results suggest that most InP-based devices under minority-carrier injection mode operation conditions are more radiation resistant than any other material-based devices.

PACS numbers: 72.20.Jv, 81.40.Ef, 61.80.Fe, 84.60.Jt

The authors have recently succeeded in fabricating a single-crystal InP n⁺-p junction solar cell having a conversion efficiency exceeding 16% at AM1.5. This highly efficient InP solar cell has also been found to be more radiation resistant than either Si or GaAs solar cells. In order to clarify the mechanism for the excellent radiation resistance of this InP solar cell, it is essential to investigate the physical aspects such as the annealing behavior for radiation-induced defects in InP.

We report here on the first observation of minority-