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Structure and growth of the interface of Pd on *a*-Si:H

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The structure of the Pd$-a$-Si:H interface is probed using interference-enhanced Raman scattering. It was found that ~ 2 nm of Pd was initially consumed to form a crystalline silicide at the Pd$-a$-Si:H interface. Annealing to 300 °C caused a spectroscopic change, which is associated with a structural change, and additional annealing at 500 °C caused the formation of crystalline Si.

An area of considerable recent interest is the characteristics of compound formation at the interface of metals on crystalline Si. It has been shown that many silicides can be formed by thermal processing at temperatures well below the eutectic temperatures in the appropriate metal-silicon binary phase diagram.[1,2] In addition many of these interfaces exhibit excellent Schottky barriers. Of technological importance is the fact that the resultant structures are stable and uniform and can be produced with little consumption of the underlying crystalline Si.[1]

The physical questions that arise concerning the silicide formation include understanding the nucleation and growth processes. It is clear that both thermodynamic and kinetic processes are involved.[1,2] With the emergence of hydrogenated amorphous Si (*a*-Si:H) as a technologically important material, similar questions of silicide formation will undoubtedly become important.[3] In addition, the kinetics involved in silicide growth at an amorphous-polycrystalline interface are certainly not obvious from the studies of crystalline silicon. In this study we address these questions. We are specifically concerned with the initial formation process and the structural changes due to thermal annealing at temperatures up to the *a*-Si:H crystallization temperature.[3]

The basic technique that is employed here to study the Pd$-a$-Si:H interface is Raman scattering. Several major difficulties exist in applying standard Raman scattering techniques to metal-semiconductor interfaces. These include illuminating a "buried" interface, collecting the scattered light and weak signal from very thin regions. To overcome these difficulties we have employed a technique termed interference-enhanced Raman scattering (IERS) which allows good sensitivity for absorbing films < 5 nm in thickness.[4-6] We have also used standard Raman scattering and Rutherford-ion backscattering to examine the Pd silicides which form on crystalline Si, and these will act as spectroscopic standards for this study.

The IERS configuration employs a multilayer sample which uses optical interference properties to achieve an enhancement of the Raman signal by a factor of 5 to 1000.[4,5] In this study a four-layer configuration was used which consisted of a lower layer of optically thick aluminum (~ 100 nm), a spacer layer of SiO_2 (40 nm), and the sample layers of *a*-Si:H (10 nm) with a very thin Pd upper layer. This configuration causes the electric field intensity due to the incident 514.5-nm laser radiation to be maximum at the Pd$-a$-Si:H interface. Thus Raman-scattered light is generated from excitations of the interface region. An important aspect of the IERS multilayer configuration is that the resultant Raman-scattered light is interference enhanced to exit normal to the film. In addition, since the films are very thin, little of the Raman-scattered light is reabsorbed. Hence the combination of these effects allows the IERS to be sensitive to interfacial structures.

The Al and SiO_2 layers used in the IERS configuration were deposited by *e*-beam evaporation, while the Pd layer was prepared by thermal evaporation. The *a*-Si:H was deposited in a separate diode configuration reactor[3] where pure silane was decomposed in a plasma with 1 W of rf power. The deposition occurred at the anode where the substrates were held at a temperature of 230 °C. Amorphous Si produced in this manner is known to exhibit a low number of electrically active defects and a hydrogen concentration of ~ 8 at. %.[3] The samples were removed from the reactor and placed in the Pd evaporator suffering an exposure to air for less than an hour.

All the annealing steps were carried out in diffusion-pumped vacuums of $\sim 10^{-6}$ torr, but most Raman measurements were done with the samples held in air with a flow of cool He gas which was used to eliminate scattering due to the molecules in the air

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and to cool the sample. All the Raman measurements were done in a backscatter configuration where 50 mW of cylindrically focused 514.5-nm Ar-ion laser radiation was incident at ~30° from the film normal, and the scattered light was collected along the normal using $F1.2$ optics. For the IERS configuration, spectra were acquired in ~20 min. For all of the samples reported here polarized spectra were obtained and several highly polarized modes were identified. The polarization properties were consistent for both the thick film and IERS corresponding structures. However, owing to the complicated nature of the spectra and the proposed crystal structures,[7] a simple group-theoretical analysis would not be definitive.

We consider first the results from the thick film standards which consisted of Pd (80.0 nm) on Si(100) wafers. To form the initial silicide a sample was annealed to 300 °C for 15 min.[2] The Rutherford backscattering (RBS) results showed that the Pd had been consumed, and a silicide formed with a composition near Pd_2Si. This measurement also indicated the presence of a Pd-rich layer at the top surface where the Pd-to-Si concentration ratio was ~2.25. The Raman spectrum of this sample is shown in Fig. 1(a). Since Pd should not exhibit first-order Raman scattering and Si exhibits a single line at 520 cm^{-1}, the sharp lines are attributed to a crystalline compound with composition near Pd_2Si. The sample was further annealed at several stages from 300 to 700 °C, and the Rutherford backscattering after the 700 °C anneal showed a compositionally uniform silicide

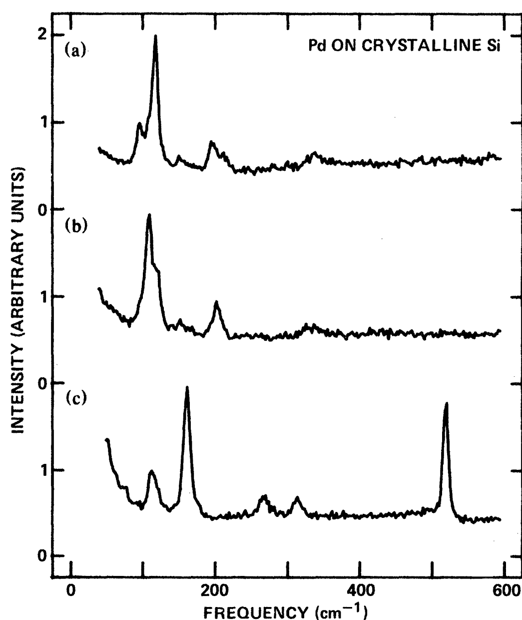

FIG. 1. Raman spectra of 80 nm of Pd on Si(100) after 15-min oven anneals at 300 °C (a), 400 °C (b), and from an electron-beam-annealed sample (c). A spectral slit width of 5 cm^{-1} was used.

which exhibited a composition of Pd_2Si. The Raman spectrum changed significantly after the first additional anneal but then remained unchanged through this thermal processing to 700 °C. A typical spectrum is shown in Fig. 1(b). We note that the groups of lines are near those of the initial silicide phase but are definitely distinct. This suggests the existence of a second phase of Pd_2Si or a similar structure with composition near this. It should be noted that there is some disagreement about the nature of the Pd-Si binary phases in the composition range near Pd_2Si.[7] Whether the new phase observed here also exists in bulk form is another interesting question.

The Raman spectrum of PdSi which can be produced by annealing at 800 °C is distinct from that of the two ~Pd_2Si phases. The RBS measurements have shown that an e-beam-annealed specimen has produced PdSi,[8] and the Raman spectrum of this sample is shown in Fig. 1(c). The line at ~520 cm^{-1} is due to crystalline Si which has formed at the surface, and the other lines are attributed to crystalline PdSi.

Consider now the interface of Pd on a-Si:H in the IERS configuration. Two samples were used: one with 2-nm Pd and the other 6-nm Pd, both on 10 nm of a-Si:H. The Raman spectra of these samples taken within 20 h after deposition were identical, and the spectrum of the 2-nm film is shown in Fig. 2(a). The broad feature at ~480 cm^{-1} is attributed to the a-Si:H film; however, the relatively sharp lines at ~110 cm^{-1} are clear indications of the presence of a crystalline compound. From comparison with Fig. 1 it is evident that this corresponds to the palladium silicide phase that forms initially on crystalline Si. Both the 2- and 6-nm Pd samples were annealed at 100 °C. The spectrum of the 2-nm Pd film showed no change, while the spectrum from the 6-nm Pd film

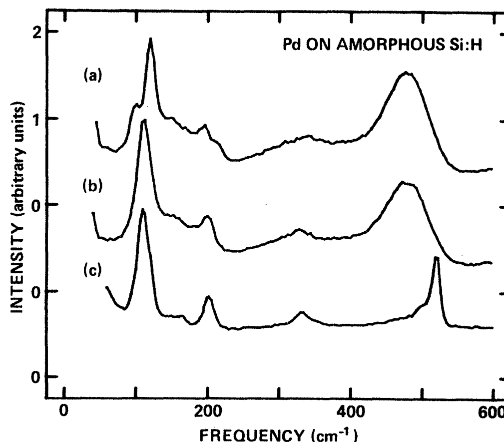

FIG. 2. Raman spectra of 2 nm of Pd on 10-nm a-Si:H in the IERS configuration. The spectra were obtained from an as-deposited sample (a), 300 °C (b), and 500 °C (c) oven anneal. A spectral slit width of 10 cm^{-1} was used.

showed a growth of the lines associated with Pd_2Si with respect to the 480-cm^{-1} *a*-Si:H line. Since the initial spectra of both samples showed an identical ratio of the intensities of the sharp lines to the broad 480-cm^{-1} line, we conclude that the same amount of silicide formed initially. Furthermore, since there was no change of the spectrum of the 2-nm film after additional annealing, it seems likely that the full 2 nm of Pd is initially consumed to form crystalline Pd_2Si. It should be noted that similar results were obtained from Pd (Refs. 9 and 10) and Ni (Ref. 11) on crystalline Si where more conventional surface analysis techniques were used.

At this point the role of impurities, in particular oxygen, should be considered. It has been reported that ~0.5 nm of native oxide forms on the *a*-Si:H film within minutes after air exposure, and prolonged air exposure does not cause significant further growth of the oxide.[12] With the preparation described here, ~0.5 nm of native oxide forms on the *a*-Si:H film before the Pd deposition. Nevertheless, it is clear that the thin oxide presence does not preclude the silicide formation. We have carried out Auger depth profiling on a sample annealed to 100 °C and found that the silicide had formed between the oxide and the *a*-Si:H layers and that the silicide-*a*-Si:H interface was oxygen free. To further explore this, Pd was evaporated on a film which had been aged in air for several weeks. The Raman spectrum of this sample showed only features associated with the *a*-Si network. Even annealing to 400 °C showed no spectral changes. Thus to form the initial silicide it is necessary to penetrate the oxide and this most likely occurs by the Pd atoms at weak or thin points. This effect appears to be inhibited by a more complete oxide coverage which results from prolonged exposure to air.

We addressed the question whether the other Pd silicides could be formed by additional annealing. The Raman spectrum of the 2.0-nm sample annealed to 300 °C is shown in Fig. 2(b). Here the silicide lines have grown dramatically. Additionally, close examination indicates that the spectrum is reminiscent of the second Pd_2Si phase which forms with annealing above 300 °C on crystalline Si. Hence here again we find an analogy with crystalline Si. We have carried out further annealing to 500 °C, and the resultant spectrum is shown in Fig. 2(c). It was hoped that the unconstrained *a*-Si network might allow formation of PdSi at a lower temperature than the 800 °C required for Pd on crystalline Si. Clearly the Pd_2Si remains, and there is no evidence of PdSi formation. However, the sharp feature at ~520 cm^{-1} indicates that the remaining *a*-Si has crystallized. This should be contrasted with the typical crystallization temperatures of *a*-Si:H of > 650 °C.[3] It is not clear whether the crystallized Si was the remaining *a*-Si layer or whether Si had diffused through the Pd_2Si and formed islands of crystalline Si. However, from experiments on epitaxial growth of Si through a Pd_2Si layer,[13] we suggest a similar phenomenon here. That is that the silicon diffuses through the Pd_2Si layer and nucleates the crystalline Si at grain boundaries and the top surface.

The role of H is certainly a significant factor for the properties of *a*-Si:H, and the hydrogen affinity of Pd suggests that the presence of this element might be important in the silicide formation process. Our measurements, however, were insensitive to any such effects. No features due to Pd–H vibrations,[14] which are expected to occur at ~490 cm^{-1}, were observed, and the 2000-cm^{-1} Si–H feature showed an expected intensity reduction with annealing for longer times and higher temperatures.[6]

The measurements presented here demonstrate that Raman scattering utilizing the IERS configuration is a useful probe of interface structures which may complement other more standard surface analytical probes. With regards to the Pd–*a*-Si:H system, several crystalline interface structures have been observed. There are, however, several unanswered questions. These include the roles of oxygen and hydrogen and more complete structural assignments. In addition, the relation of the interface structures to the Schottky barrier properties is an important area which we are only beginning to explore.

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