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SILICIDE FORMATION AT THE INTERFACE OF Pd ON AMORPHOUS AND CRYSTALLINE Si

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Raman scattering and Rutherford backscattering are combined to study silicide formation at the interface of Pd on crystalline or hydrogenated amorphous Si (a-Si:H). The Rutherford backscattering measurements are used to determine the composition of the silicides formed after different thermal annealing. Usual backscatter Raman spectra indicate two phases of Pd_2Si composition. The Raman spectrum of PdSi is also reported. The interference enhanced Raman scattering sample configuration is applied to Pd on a-Si:H, and it is found that ~20Å of Pd_2Si forms immediately after deposition. The silicide grows and changes phases as the sample is annealed to ~300°C. Aspects related to aging are also discussed.

Introduction

Despite the importance of the metal-semiconductor interface in most semiconductor devices, many questions remain concerning the fundamental aspects of the atomic scale structure at the interface. The metal-silicon interaction at low temperatures, which often leads to the formation of various silicides, is believed to play an essential role on Schottky barrier device properties. In addition, hydrogenated amorphous silicon (a-Si:H) has been the subject of many studies primarily because of its potential in solar cell and other large scale device applications. Even less is known about the metal-amorphous Si interface. In this study both usual backscatter Raman spectroscopy and interference enhanced Raman scattering (IERS)[1] are coupled with Rutherford backscattering spectroscopy (RBS) to investigate the interfacial Pd-silicide structure and growth properties on a-Si:H and crystalline silicon.

Experiment

When the IERS sample configuration is used Raman backscattering becomes a surface-sensitive technique because very thin films are used and thus the surface or interface yields a significant contribution to the spectrum. A schematic of the four-layer IERS sample configuration used in this study is shown in Fig. (1). A very thin (20-60Å) Pd film is thermally evaporated onto a layer of 100Å-thick plasma-deposited a-Si:H film, which lies on top of a transparent SiO_2 spacer and an Al reflector. The thicknesses of the layers are adjusted so that an antireflection condition is achieved

through destructive interference. Most of the incident radiation is thus absorbed by Pd and a-Si:H. Furthermore, the Raman scattered light suffers relatively little reabsorption in the thin films, and the same interference conditions also give rise to a constructive interference of the normally exiting scattered radiation. Using this technique Raman spectra can be obtained from very thin films with intensities enhanced over that from the corresponding bulk samples.

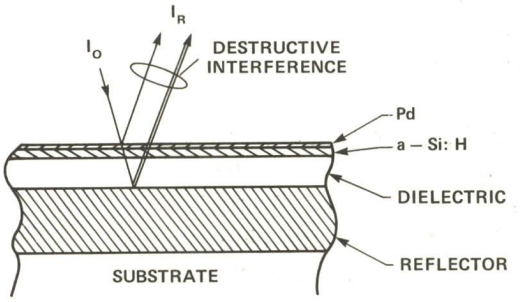

Figure 1 A schematic of the four-layer IERS sample configuration. The thicknesses of the Pd, a-Si:H, and SiO_2 layers used are 20-60, 100, and 400Å respectively, such that an antireflection condition is obtained for the incident 5145A Ar ion laser radiation, Io.

The a-Si:H films used in the IERS samples were deposited in pure SiH_4 plasma from the anode of a diode system [2] at a low rf power of 1W and a substrate temperature of 230°C. Such films contain ~8 at .% hydrogen. These samples were then transported to an evaporation chamber for the Pd deposition. The substrates were mounted ~40 cm away from the resistively heated Pd wire to minimize sample heating during evaporation. Thick films are required in both the usual Raman scattering and the RBS studies. For the experiments described here 1000A Pd films were evaporated in an oil-free vacuum system onto n-type (100) Si wafers.

Results and Discussion

Consider first the properties of Pd on (100) Si. Previous studies [3] have shown that annealing at ~300°C causes the formation of Pd_2Si at the interface. Raman and RBS measurements have been carried out on a sample annealed in vacuum for 15 minutes at 300°C. The RBS measurements indicate that the Pd layer is consumed, and a silicide forms with composition near Pd_2Si. The measurement indicates the surface may be slightly Pd-rich. Raman spectra of this film are shown in Fig. (2a). The relatively sharp features at 97, 119, 198, 212 and 338 cm^{-1} are attributed to the Pd_2Si crystal structure. Further annealling at this temperature for a total of 30 minutes or at 400°C for 20 minutes causes notable changes in the Raman spectrum as shown in Fig. (2b). The most obvious is the growth of a strong feature at 110 cm^{-1}. RBS, however, still gives a composition of Pd_2Si. This indicates that associated with Pd_2Si there are two separate crystal structures, each of which has a different signature in the Raman spectrum.

To examine the high temperature Pd-silicide, an electron-beam annealed sample was also investigated in which RBS measurements indicated a composition of near PdSi. Studies have indicated that PdSi exhibits an orthorhombic, MnP-type crystal structure [4] which forms at a relatively high temperature of ~800°C [3]. The Raman spectrum of this sample is shown in Fig. (2c). The line at ~520 cm^{-1} is due

to crystalline Si while the other features are attributed to PdSi. We note the strong line at 162 cm^{-1} clearly distinguishes PdSi from the two structures of Pd_2Si.

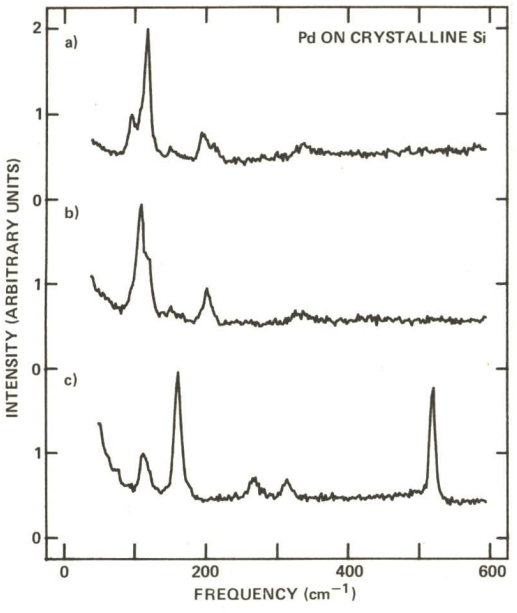

Figure 2 The $I_{\parallel\parallel}$ Raman spectra of 1000A Pd on (100)Si obtained after vacuum furnace annealing at 300°C for 15 minutes, (a), and 400°C for 20 minutes, (b), and after electron beam annealing, (c)

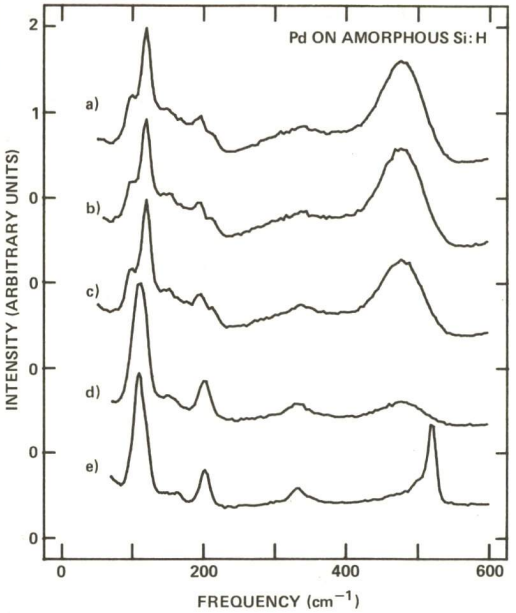

Figure 3 Raman spectra of as-deposited Pd on a-Si:H with 20Å, (a), and 60Å, (b), of Pd. Curves (c) and (d) represent the latter after 15 minute annealing at 100 and 300°C, respectively. Curve (e) is the spectrum obtained after annealing the 20Å Pd sample at 500°C for 2 hours.

Consider now the interface between Pd and a-Si:H which we study using the IERS sample configuration. Fig. (3a) shows the Raman spectrum obtained ~20 hours after 20Å of Pd was deposited. Comparison with Fig. (2a) shows that sharp lines associated with the first Pd_2Si crystal structure are already present. In addition, the broad peak at ~480 cm^{-1} is due to the a-Si network. To determine the extent of silicide formation, 60Å of Pd was deposited on a-Si:H at the same time as the 20Å deposition and the resultant Raman spectrum is shown in Fig. (3b). We note that the ratio of the intensity of the 119 and 480 cm^{-1} peaks in both as-deposited samples is identical. Both samples were annealed in vacuum at 100°C for 15 minutes. The Raman spectrum of the 20Å Pd sample showed no change while for the 60Å Pd sample, as shown in Fig. (3c), the 119 cm^{-1} line grew relative to the 480 cm^{-1} line. These measurements indicate that in both samples the initial silicide formation consumed ~20Å of Pd to form Pd_2Si. Recent results have shown similar Pd_2Si formation on crystalline Si[5].

To determine whether the second Pd_2Si phase could be obtained, samples

were annealed at 300°C for 15 minutes. The resultant spectrum shown in Fig. (3d) clearly indicates the formation of the second Pd_2Si phase. We note that while aging the sample at room temperature caused continued growth of the first Pd_2Si phase, the second phase was not observed even after several months.

We attempted to produce the PdSi phase by annealing the 20Å Pd sample at 500°C, and the resultant spectrum is shown in Fig. (3e). Here the features due to the second Pd_2Si phase remain but the broad 480 cm^{-1} a-Si feature is replaced by a sharp line at 520 cm^{-1} that is attributed to crystalline Si. We note that a-Si:H must normally be annealed to ~700°C before crystallization occurs.

In the experiments on a-Si we emphasized that the Pd deposition occured within hours of the a-Si:H deposition. To examine aging effects we repeated the Pd deposition on a-Si:H samples that were stored for several months. The Raman spectra showed only features attributed to a-Si and even heating to 400°C caused no evidence of silicide formation.

Conclusion

When Pd is deposited onto freshly prepared a-Si:H, even at the room temperature, a very thin layer of ~20Å of crystalline Pd_2Si forms at the interface within a few hours. This does not happen, however, on aged a-Si:H. Moreover, the growth of Pd_2Si continues with time at a slow rate. These could make significant impacts on the property, as well as the stability of Schottky barriers. In addition, a second Pd_2Si phase is observed which forms at 300-400°C on either crystalline or amorphous Si.

This study demonstrates that Raman scattering can be a useful and non-destructive tool to investigate the silicide formation at an interface. When the IERS method is employed, this structural probe becomes a surface or interface sensitive technique which can study the formation of ~5Å silicide at the interface.

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