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Effect of interfacial hydrogen in $CoSi_2$/Si(100) Schottky-barrier contacts

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We have studied the effect of hydrogen in the $CoSi_2$/Si(100) interface on the Schottky-barrier height of $CoSi_2$ on n-type and p-type Si(100). It was found that hydrogenation results in an increase of 120 meV in the barrier height to n-type Si(100). Measurements of the hydrogen concentration in the interface, using quantitative ion-beam techniques, were used to establish the correlation between the change in barrier height and hydrogen concentration; other hydrogen effects such as passivation of shallow donor and acceptor impurities in silicon were ruled out. The results demonstrate that 8×10^{15} hydrogen atoms/cm^2 can alter an interface layer and thereby change the pinning position of the Fermi level.

There is still much controversy about the various models proposed to date to explain the formation of Schottky barriers at metal-semiconductor (MS) interfaces. Deviations from Schottky's model for the origin of the barrier height as the work-function difference between the metal and semiconductor were first explained with interface states by Bardeen[1] who attributed them to intrinsic states of the clean semiconductor surface. More recently, new models[2] have been proposed based on Fermi-level pinning by states intrinsic to the interface. According to these models, the Schottky-barrier height (SBH) is determined by the virtual gap states (VGS) of the complex band structure of the semiconductor, and deviations from the charge neutrality level of the VGS are attributed to the M-S electronegativity difference. Other models[3] of barrier formation have been proposed based on pinning by states associated with defects created in the semiconductor band gap at or close to the interface during its formation. One approach to examining the role of interface states in barrier formation is to introduce hydrogen into the interface because of its ability to passivate these states, or to alter their density and distribution, and to look for any resulting change in the barrier height.

There have been numerous previous attempts to detect a change in SBH after hydrogenation. Unfortunately, hydrogenation can produce other effects which also change the SBH significantly. For example, where hydrogen has been introduced by ion implantation,[4,5] the observed effects are dominated by radiation damage in the semiconductor. In many studies,[6,7] hydrogen has been found to diffuse into the silicon substrate and passivate shallow donor and acceptor impurities there. Passivation of a near-surface layer of dopants causes an increase in the measured SBH on both n-type and p-type substrates,[8–11] in the same way as deliberate compensation of the dopants does.[12] Thus in searching for a true interface effect, it is extremely important to avoid passivation of dopants in the substrates.

In the present work we have introduced hydrogen into the interface of polycrystalline $CoSi_2$ on n-type and p-type Si(100) using techniques that leave the interface undisturbed, except for the introduction of hydrogen. We have measured the interface hydrogen content using quantitative ion-beam techniques. We present results that show that a sufficient amount of hydrogen in the interface can cause an increase of 120 meV in the SBH to n-type Si(100) and that this increase is not due to hydrogen passivation of shallow donor impurities in silicon.

Formation of polycrystalline $CoSi_2$ layers was carried out by deposition of 500-Å-thick cobalt layers onto Czochralski (100)-oriented silicon wafers (doped with either phosphorous or boron to a concentration of $10^{14}-10^{15}$/cm^3) and subsequent annealing at 650 °C for 30 min. To minimize contamination of the $CoSi_2$/Si(100) interface, a clean hydrogen-terminated surface was formed on the Si wafers[13] immediately before they were inserted into the deposition system. X-ray diffraction and Rutherford backscattering spectrometry (RBS) measurements confirmed that a stoichiometric layer of $CoSi_2$ had formed after the anneal. The thickness of the $CoSi_2$ layers was $\sim$1400 Å as measured by RBS. For electrical measurements diodes of 0.75 and 1 mm in diameter were formed by covering part of each wafer by a metal mask during the Co deposition.

Deuterium was introduced into the surface of the $CoSi_2$ layers by implantation at an energy of 200 eV for 2 h at 98 °C. Patterned and unpatterned pieces of both n-type and p-type samples were placed together on a heated platen, which was biased at -200 V with respect to an intense deuterium plasma generated by an electron cyclotron resonance microwave ion source. The deuterium profiles were measured using secondary ion mass spectrometry (SIMS) and the amount of deuterium in the interface was quantified by forward recoil detection (FRD) with a 2.3% MeV He beam.[14] In these measurements the He beam was incident at an angle of 8° to the sample surface, and recoiling hydrogen was detected at a scattering angle of 30°.

Schottky-barrier heights for as-grown and hydrogenated samples were determined using current-voltage (I-V), capacitance-voltage (C-V), and photoelectric measurements at temperatures in the range 77–300 K. Because of the low barrier heights to p-type Si(100) these measurements were performed at temperatures below 250 K. To check for passivation of shallow dopants in the Si substrate, the electrically active donor and acceptor concen-

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tration depth profiles were measured. At depths between the $CoSi_2$/Si(100) interface and the depletion depth (typically $\sim 0.5-1$ μm under zero bias) these were measured using a spreading resistance technique and at greater depth by C-V profiling.

Figure 1 shows a SIMS depth profile of the hydrogen content of two samples, one grown on n-type and the other on p-type Si(100). In both samples there is clearly deuterium trapped in the $CoSi_2$/Si(100) interface. Also, as can be seen in Fig. 1, there is a large peak near the surface, corresponding to deuterium trapped at defects produced by implantation. The amount of deuterium in the $CoSi_2$/Si(100) interface was quantified with FRD. Figure 2 shows FRD measurements of these samples, together with fits made with the RUMP analysis program.[15] Because the heavier deuterium (^{2}H) recoils with higher energy than ordinary hydrogen (^{1}H) at the same depth, the profile of ^{2}H is shifted up in energy relative to that of ^{1}H. The figure shows peaks corresponding to the near-surface layer of implanted deuterium and to the deuterium in the interface of the n-type samples, as well as ^{1}H on the surface. The near-surface deuterium is well fitted by depth profiles consisting of a half Gaussian with a half-width at half maximum of 425 Å and areas of 4×10^{16} and 3×10^{16} ^{2}H/cm^2 for n-type and p-type samples, respectively. Since the projected range and straggling of 200 eV ^{2}H in $CoSi_2$ are calculated to be 24 and 38 Å, respectively, some diffusion of the implanted ^{2}H must have taken place during the plasma treatment. A fraction of the implanted deuterium diffused to the $CoSi_2$/Si(100) interface and was trapped there. The trapping enthalpy has been measured[16] to be 0.91 eV. Similar observations have been made in the Al/Si(111) system.[17] In the n-type samples studied here the amount of deuterium in the interface was 8×10^{15} atoms/cm^2 after implantation, and the amount in the p-type samples was too low to be registered by FRD. However, if we assume that the SIMS deuterium signal was linear with interface concentration, then scaling the date in Fig. 1 gives a concentration of $\sim 4\times10^{13}$ atoms/cm^2. This is probably due to a lower sample temperature during the implantation treatment. Thus these two samples give us an opportunity to compare the effects of large and small amounts of hydrogen. It should be noted here that the SIMS signal for ^{2}H in the Si substrates (Fig. 1) is at the background level. The spreading resistance measurements described below provide a much more sensitive test for hydrogen in the silicon.

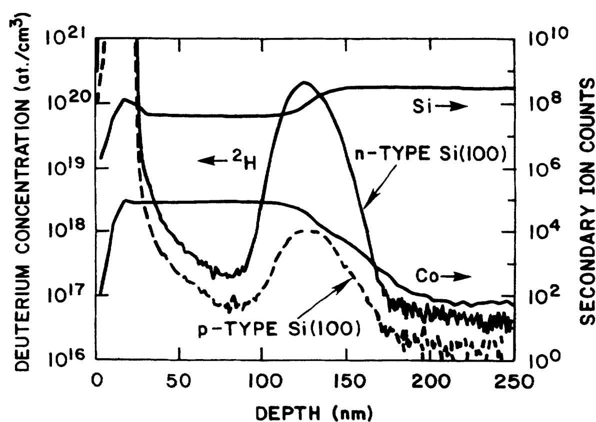

FIG. 1. SIMS profiles of deuterium and silicon in deuterated samples formed on n-type and p-type Si(100).

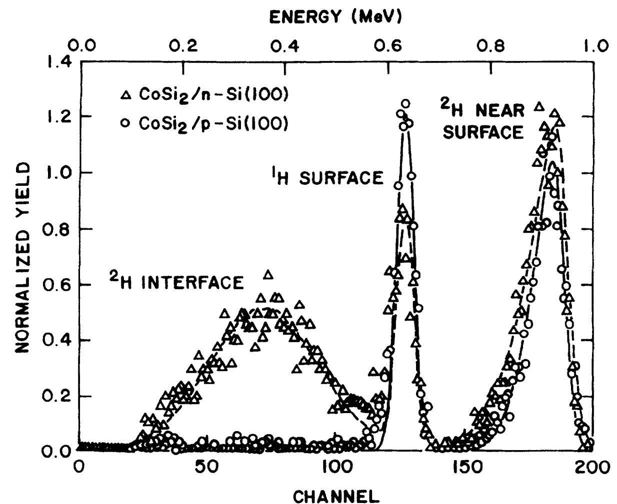

FIG. 2. Hydrogen and deuterium depth profiles in deuterium-implanted samples, measured by FRD. Data from samples formed on n-type and p-type Si(100) are shown. The peaks corresponding to near-surface implanted deuterium, surface hydrogen, and deuterium in the $CoSi_2$/Si(100) interface are labeled. Note that the amount of interface ^{2}H in the p-type samples is much less than in the n-type samples.

The C-V characteristics plotted in Fig. 3 show examples of the results obtained for the n-type samples before and after hydrogenation. The I-V characteristics of the n-type samples yielded ideality factors $n=(q/kT)(\partial V/\partial \ln J)$ of 1.02–1.03 and barrier heights at 295 K, using a Richardson constant of 112 A K^{-2} cm^{-2}, of 0.63 and 0.75 eV before and after hydrogenation, respectively. For the p-type samples, on the other hand, the I-V characteristics yielded ideality factors of ≤ 1.05 and a barrier height at 225 K, using a Richardson constant of 32 A K^{-2} cm^{-2}, of 0.45 eV which remained very little affected by hydrogenation. These barrier height values are in very good agreement with those deduced from the C-V measurements and from photoelectric measurements performed on some samples.[18]

In the n-type samples, no passivation of phosphorous donors occurs after hydrogenation as revealed by C-V profiling. In Fig. 4 we show free-carrier concentration profiles obtained from spreading resistance measurements at 295 K for the n-type samples before and after hydrogenation. These measurements were made under the same $CoSi_2$ contacts used for SBH determination. The $CoSi_2$ was removed by a chemical etch before the measurement. The profiles under the hydrogenated and nonhydrogenated $CoSi_2$ contacts are identical within the scatter of the data showing no phosphorus passivation near the interface. In contrast, the profile from an exposed region of Si between the $CoSi_2$ contacts in the hy-

drogenated samples shows partial passivation of the phosphorus donors.[7] For the *p*-type samples, these measurements also show a negligible degree of passivation of boron acceptors in the Si substrate under the $CoSi_2$ contacts as illustrated in Fig. 5. Contrasted to this, the profile from an exposed region of Si between contacts in the hydrogenated sample shows extensive boron passivation which extends to a depth of up to 6 μm in the bulk, with the near-surface concentration reduced by more than two orders of magnitude. Thus, it can be seen from Figs. 4 and 5 that hydrogen diffusion through the $CoSi_2$/Si(100) interface into *n*-type and *p*-type silicon does not take place.

Our results clearly demonstrate that hydrogenation results in an increase of 120 meV in the SBH of $CoSi_2$ on *n*-type Si(100) and that this increase is not due to hydrogen passivation of phosphorus donors in silicon. Mechanisms whereby the interface hydrogen can alter the barrier height include altered interface dipole, passivated defects, altered metal work function, altered charge neutrality level, and altered interface states. The amount of hydrogen localized at the interface for *n*-type Si(100), 8×10^{15} ^{2}H/cm^2, is substantially larger than needed for a monolayer [the Si(100) monolayer density is 6.8×10^{14} atoms/cm^2]. This means that to limit the discussion to an altered interface dipole of passivated interface defects or interface states would not account for most of the hydrogen. Aspnes and Heller[19] have shown that hydro-

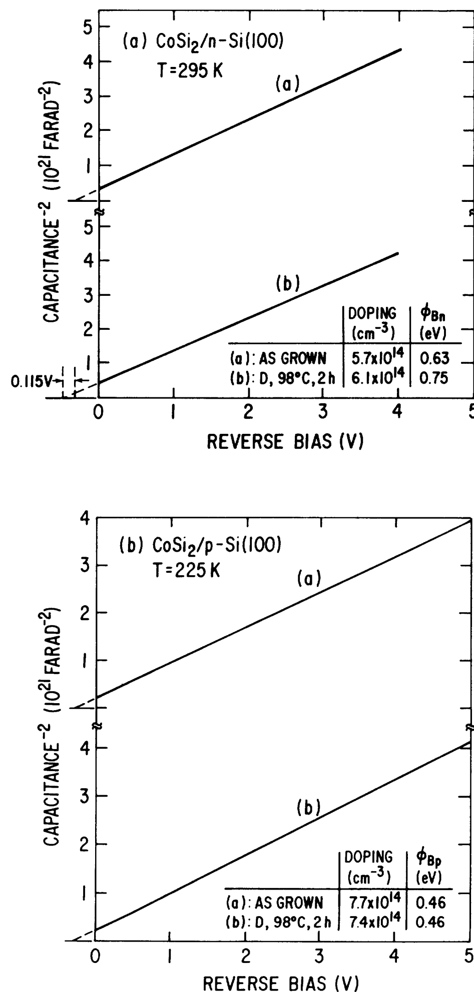

FIG. 3 Capacitance-voltage characteristics of $CoSi_2$ on (a) *n*-type and (b) *p*-type Si(100) before and after hydrogenation. Measurements are performed at a frequency of 1 MHz. The diode area is 4.56×10^{-3} cm^2.

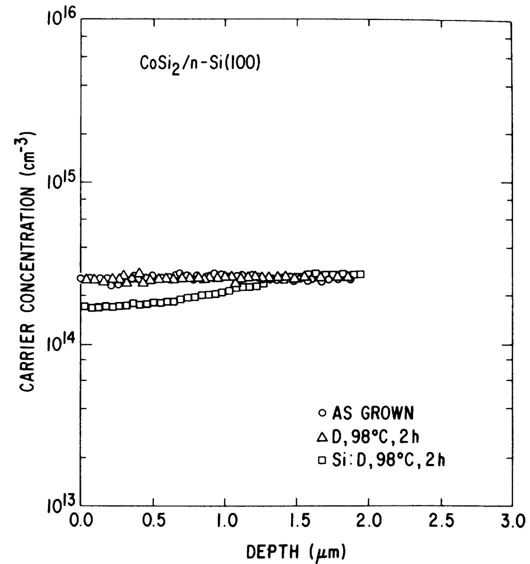

FIG. 4. Active carrier concentration depth profiles obtained by spreading resistance measurements for *n*-type samples before and after hydrogenation. These are compared with the profile from an exposed region of Si between the $CoSi_2$ contacts in a hydrogenated sample, which is the only one to show partial passivation of the phosphorus donors in silicon.

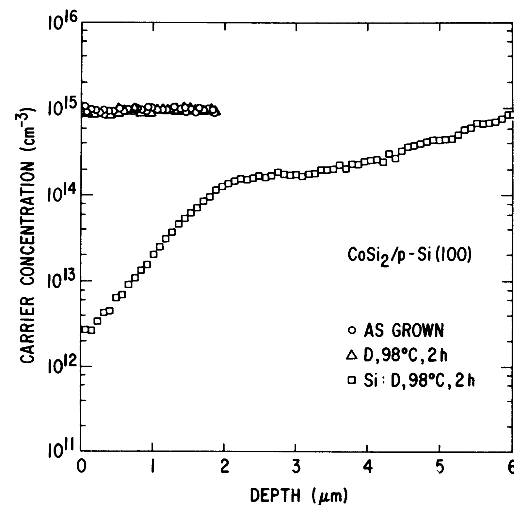

FIG. 5. Active carrier concentration depth profiles obtained by spreading resistance measurements for *p*-type samples before and after hydrogenation. These are compared with the profile from an exposed region of Si between the $CoSi_2$ contacts in a hydrogenated sample, which is the only one to show extensive passivation of the boron acceptors in silicon.

genation of bulk platinum-group metals tends to reduce the work function; if true also for $CoSi_2$, then the sign of the altered barrier height suggests that a changed metal work function is not responsible for the increased barrier height upon hydrogenation. An altered interface layer of $\simeq$10-Å thickness is consistent with the amount of hydrogen present in the interface. Aboelfotoh[20] and Fujieda[21] have shown that interlayers can have a strong effect on interface band line-ups. Freeouf *et al.*[22] have shown that such an interface layer can change the Fermi-level pinning position from that of the bulk semicondutor to one representative of the new interface material. A silicon hydride may well have a charge neutrality position that is different from that of Si; a sufficiently large band gap could even exhibit no Fermi-level pinning at all, as shown by Wittmer and Freeouf[23] for nonreactive contacts on hydrogen-passivated silicon.

Our results, on the other hand, show that the barrier height to *p*-type Si(100) is very little affected by hydrogenation. The amount of hydrogen in the interface between $CoSi_2$ and *p*-type Si(100) is only $\sim 4\times 10^{13}$ $^2H/cm^2$. This would correspond to a uniform layer of thickness $\lesssim 0.1$ Å, which is both unrealistic (given atomic dimensions) and too thin to decouple the wave functions of the metal electrons from those of the semiconductor; thus, the charge neutrality level of bulk silicon would apply. The alternative is to have thick patches of altered material dispersed in an otherwise intimate contact. The amount of hydrogen suggests that only a small area can have this altered material ($\lesssim 10\%$); again, the interface properties must be dominated by the intrinsic regions, as shown experimentally. Our results thus suggest that this altered interface layer plays an important role in controlling the pinning position of the Fermi level. For example, within the framework of the Tersoff[22] model, it must alter the charge neutrality level from that of the bulk silicon.

In summary, we have shown that the presence of 8×10^{15} hydrogen atoms/cm^2 in the $CoSi_2$/Si(100) interface causes an increase of 120 meV in the barrier height to *n*-type Si(100). Measurements of the hydrogen contraction in the interface were used to establish the correlation between the change in barrier height and hydrogen concentration, and other hydrogen effects such as passivation of shallow donor and acceptor impurities in silicon were ruled out. Therefore, we have demonstrated that a sufficient amount of hydrogen can alter an interface layer and thereby change the pinning position of the Fermi level.

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