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Formation and decomposition of hydrogen-related electron traps at hydrogenated Pd/GaAs (*n*-type) Schottky interfaces

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We demonstrate a capability for exploring the behavior of hydrogen at a Pd/GaAs (*n*-type) Schottky interface containing a native oxide. By applying a large forward current to such a hydrogenated interface, a remarkable reduction of the hydrogenation effect was observed. Formation of hydrogen-related electron traps near the interface could be responsible for this reduction of hydrogenation effect. Moreover, evidence was observed for the decomposition of those electron traps when hydrogen was forced to diffuse out from such interfaces. © *2000 American Institute of Physics.* [S0021-8979(00)04909-4]

I. INTRODUCTION

The adsorption of hydrogen on solid surfaces of transition metals has been extensively investigated.[1] On Pd surfaces, hydrogen is found to dissociate to atomic hydrogen which diffuses into the bulk of the metal; this results in a change in the electrical properties of the Pd/oxide/semiconductor interface.[2] This change is reversible during cycles of hydrogenation and dehydrogenation,[2] corresponding to a process where the device is cyclicly exposed to hydrogen ambience and oxygen ambience. It is known that there is an increase or decrease in the barrier height for the hydrogenated *n*-type or *p*-type Schottky interfaces, respectively.[3–5] This change of barrier height is believed to result from the formation of an effective dipole layer, which is effectively positive charge, induced by hydrogen at the Pd/oxide interface.[2] This formation of a dipole at the interface is considered as an *s*-type hydrogen adatom which locates interstitially on the Pd surface and is not bounded to any fixed Pd atoms and can be considered a special case of a proton.[6] There have been reports of the hydrogenation and dehydrogenation performance of Pd/semiconductor devices for sensing hydrogen gas or for exploring the mechanism of water formation on Pd surfaces.[3–7] In addition, the presence of interfacial hydrogen has been used in studies of metal/semiconductor reactions.[4,5,8] In a Pd/GaAs Schottky interface with a thin native oxide on the GaAs substrate, electrical properties have been shown to be sensitive to the presence of interfacial hydrogen.[4,5] This provides a convenient probe for exploring the interaction between the hydrogen and electrons at Pd/oxide interfaces.

Other studies of interfacial hydrogen have used Fowler–Nordheim injection of hot electrons through a metal/SiO_2/Si interface to induce hydrogen-related interface states.[9–12] Also, plasma hydrogen implanted into Si and GaAs is found to compensate acceptors.[13–15] In those cases, source of hydrogen is considered to be involved in trap formation at the interface of the Si/SiO_2 and the carrier center compensation in the semiconductor bulk. In this article, we report a new phenomenon at hydrogenated Pd/GaAs Schottky interfaces where an interaction occurs between the hydrogen accumulated at the interface and the electrons flowing from the semiconductor through the interface. This flow of electrons is caused by a forward bias voltage applied to the interface, lowering the potential barrier for electrons in the conduction band of the semiconductor. An apparent reduction is observed in the hydrogen induced interfacial charge during such large forward currents flow. The unique approach which we used to investigate this phenomenon was to remove the hydrogen from the Pd film after the forward current flow so that not only the formation of electron traps but also the decomposition of these electron traps were examined. Measurement of capacitance changes showed evidence for a direct relationship between the presence of hydrogen and the formation of electron traps caused by forward current flow.

II. EXPERIMENT

Thin films of Pd with a thickness of ~15 nm and a diameter of 500 μm were formed by evaporating palladium in high vacuum on a vapor phase epitaxially (VPE) prepared single-crystal *n*-type GaAs(100) substrate with a carrier concentration of $2-3\times10^{15}$ cm^{-3}. Prior to the Pd deposition, the GaAs surface was treated in an H_2SO_4:H_2O_2:H_2O solution, which results in a formation of a native oxide on the surface. For comparison, a GaAs surface free of oxide was also prepared by immersing the substrate in a $(NH_4)_2S_x$ solution. This treatment results in a GaAs surface covered with an atomic layer of sulfur instead of a native oxide.[16] Therefore, we prepared two types of Pd/GaAs Schottky interfaces; one with a native oxide layer and the other with no oxygen at the interface. In this article, unless specifically described, the Pd/GaAs Schottky interface refers to the one with a native oxide layer. The Pd/GaAs Schottky interface without an oxide layer was used to confirm that there are no deep levels in the GaAs substrate used in this study. Details of the GaAs surface treatments and Pd/GaAs Schottky structure preparation was described elsewhere.[4]

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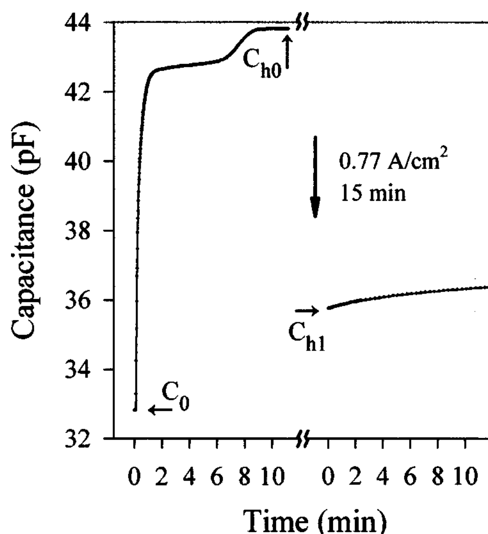

FIG. 1. Capacitance variance of a Pd/GaAs (*n*-type) Schottky interface caused by hydrogenation followed by applying a forward current at 0.77 A/cm^2 for 15 min. The initial and hydrogenated capacitances are indicated by C_0 and C_{h0}. The capacitance after the forward current flow action is indicated by C_{h1}.

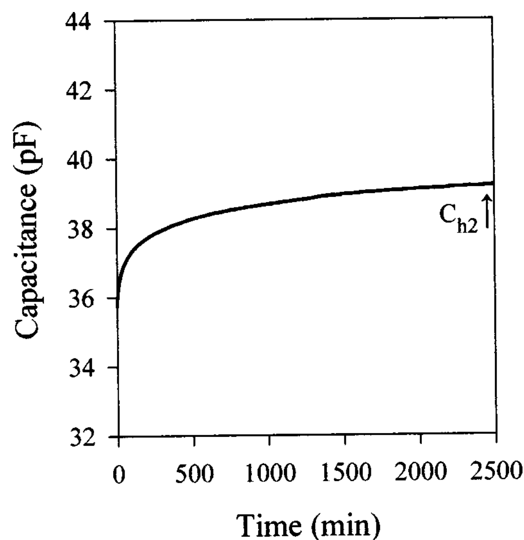

FIG. 2. Capacitance variation against time for the Pd/GaAs (*n*-type) Schottky interface in hydrogen gas after applying a forward current at 0.77 A/cm^2 for 15 min. The capacitance increased to C_{h2} after being kept in the hydrogen gas for 2500 min.

The electrical property reported in this study was capacitance measured at zero bias voltage with a capacitance meter at a frequency of 1 MHz. The capacitance is a reflection of the effective charge at the interface (at the metal side) balanced by the space charge in the semiconductor. In the case of the *n*-type semiconductor, the space charge (donor) will decrease if the negative charge at the metal side decreases, resulting in an increase in capacitance or a decrease in Schottky barrier height.[4,17]

The hydrogenation was performed by flowing hydrogen gas into an evacuated sample chamber. The pressure of the hydrogen gas increased rapidly to ~1 atm. Electrons flowing through the Schottky interface was controlled with a personal computer by changing the voltage applied between the Pd/GaAs interface so as to maintain a constant forward current through the interface with an electrometer. The current was applied to the hydrogenated Pd/GaAs (*n*-type) Schottky interface for a certain period of time at a density of 0.77 A/cm^2; this is larger than the largest current usually used to measure the barrier height in current–voltage measurement.[4] The dehydrogenation was done by evacuating hydrogen gas and consequentially exposing the system to air. All experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the variation in capacitance of a Pd/GaAs Schottky interface caused by hydrogenation and then by applying a large forward current through the interface. After exposure to hydrogen gas at ~1 atm, within 10 min the capacitance increased to ~44 pF (C_{h0}) from its initial value of ~33 pF (C_0). A minor increase of ~1 pF is observed before the capacitance approaches to saturation. Because this step-like increase of capacitance was usually observed for aged samples, its behavior may be explained by effects from surface contamination. It is known that surface contaminants could block the Pd surface for hydrogen adsorption to inhibit hydrogen passage.[18] After the capacitance became stable, a forward current with a density of 0.77 A/cm^2 was applied to the interface for 15 min. When the forward current charge was completed, the capacitance was monitored again and found to have decreased to ~36 pF (C_{h1}). On the other hand, we confirmed that when flowing a reverse current of the same order of the forward current described above, no variation in capacitance was observed.

A notable feature seen in Fig. 1 is that the increase of capacitance after the electron flow occurs extremely slowly, compared with that for hydrogenation, where the capacitance increased ~11 pF in 10 min. In contrast to this increase of ~11 pF in capacitance during the hydrogenation, in the same time period of 10 min, the capacitance only increased by 0.2 pF after forward current flow. Figure 2 shows the extremely slow increase in capacitance of the sample kept in hydrogen gas. The capacitance only increased to ~39 pF (C_{h2}) in 2500 min. Because the sample was kept in hydrogen ambience all the time, this extremely slow increase in capacitance excludes the possibility of a simple removal of the interfacial hydrogen being responsible for the decrease in capacitance by forward current flow.

In order to examine whether the observed phenomenon is due to deep levels in GaAs and/or oxide/GaAs interface traps, we conducted the following two experiments in air. A Pd/GaAs Schottky interface without an oxide layer was used in the first experiment to determine whether there are any deep levels that respond to forward current flow. Because of the absence of oxygen at the GaAs surface, Pd reacts easily with GaAs, resulting in an interface without oxide.[4] The same amount of forward current (0.77 A/cm^2) as used in Fig. 1 was applied to this interface for 15 min. No changes in capacitance were observed. This experimental fact clearly demonstrated that there were no deep levels in the GaAs

substrate that could influence the capacitance of the Schottky interface by the large forward current flow.

Knowing that there were no deep levels in the GaAs substrate, we conducted the second experiment which was designed to investigate the effect of intrinsic interface traps in the oxide on the capacitance change shown in Fig. 1. By applying the same amount of forward current (0.77 A/cm^2) to the Pd/GaAs Schottky interface with a native oxide layer at the interface in air (i.e., without hydrogenation) for 15 min, we observed only a minor decrease of $\sim$1 pF in capacitance. Because this experiment was done in air, the change in capacitance could be explained by a charge-up effect[9,19] introduced by current flow through the oxide layer at the interface. Moreover, for this sample, by introducing hydrogen gas and consequently applying the forward current to the interface, we observed a similar hydrogenation and dramatic capacitance reduction as those shown in Fig. 1, except for an offset of the $\sim$1 pF. With such a minor effect on the capacitance change, therefore, it is clear that the intrinsic interface traps in the oxide cannot explain the decrease in capacitance shown in Fig. 1.

Because it is the forward, not the reverse current flow, which changes the capacitance of the hydrogenated Pd/GaAs Schottky interface, the decrease of capacitance due to the forward current flow as shown in Fig. 1 can be considered analogous to a formation of hydrogen-related electron traps. We will first discuss the mechanisms of electron trapping. Electrons moving through a metal/semiconductor interface could be trapped by electron traps whose energy levels are below the Fermi level of the semiconductor. A forward bias voltage applied to the Pd/GaAs Schottky interface results in a higher Fermi level[17] of GaAs at the interface compared to that of Pd and lowers potential barrier for electrons to move to the Pd from the conduction band of GaAs. This action would result in the decrease in capacitance as observed in Fig. 1. We have shown that the intrinsic interface traps in the oxide themselves could only account for a minor part of the decrease in capacitance as observed in Fig. 1. Therefore, hydrogen at the hydrogenated Pd/GaAs interface has to be involved in the formation of the electron traps responsible to the observed decrease in capacitance. It is clear, therefore, that the forward current flow results in both the formation of hydrogen-related electron traps and their trapping of electrons.

Having excluded the two ''conventional'' possibilities described above for the decrease in capacitance of the hydrogenated Pd/GaAs Schottky interface, we now will propose an alternative mechanism for the formation of hydrogen-related electron traps at the interface. The hydrogenation of Pd/GaAs interface was usually stable if the temperature and the hydrogen ambience did not change (i.e., equilibrium state). However, an *s*-type hydrogen adatom is not bound to any fixed host atoms.[6] It has, therefore, ability to move if there were certain disturbance applied to the equilibrium state. An example is the dehydrogenation of the hydrogenated Pd/GaAs interfaces when they are exposed to oxygen ambience or heated in vacuum.[3,4]

From our experimental results, it is apparent that the forward current flow changes the charge state at the hydrogenated Pd/GaAs Schottky interfaces. The variation in capacitance caused by forward current flow shown in Fig. 1 could be explained by the displacement of the hydrogen into the native oxide layer of the GaAs surface where the hydrogen forms electron traps (probably with other elements) and traps electrons. The driving force for the movement of hydrogen into the oxide layer could be the electric field at the interface caused by the applied forward bias voltage.

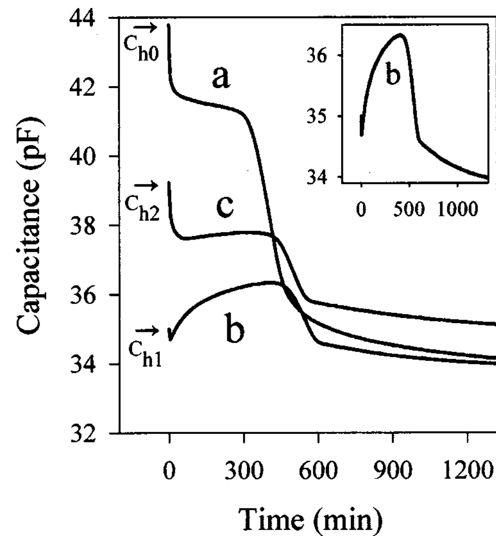

FIG. 3. Capacitance variation of hydrogenated Pd/GaAs (*n*-type) Schottky interfaces exposed to air (dehydrogenation). Three curves in the figure show capacitance monitored for: (a) a hydrogenated sample, (b) a hydrogenated sample experienced a forward current at 0.77 A/cm^2 for 15 min, and (c) a hydrogenated sample experienced a forward current at 0.77 A/cm^2 for 15 min and then kept in hydrogen gas for 2500 min. The starting values of capacitance for the three samples are indicated by C_{h0}, C_{h1}, and C_{h2}, as described in Figs. 1 and 2. The insert is used to emphasize the peak feature in curve (b).

Having proposed that the forward current flow results in the formation of hydrogen-related electron traps at the hydrogenated Pd/GaAs interface, we noticed that the reverse process, i.e., decomposition of these traps, would provide more insight into the formation of the electron traps. Thus, we conducted an experiment to expose the system to air so as to force the hydrogen to withdraw from the interface and the Pd film. Curve (a) in Fig. 3 shows the capacitance variation of a conventional hydrogenated sample after the sample was exposed to air (i.e., dehydrogenation). Two other hydrogenated samples were given a forward current at 0.77 A/cm^2 for 15 min to see the dehydrogenation difference compared to that for the conventional one shown in curve (a). Curve (b) in Fig. 3 shows capacitance variation of the sample exposed to air immediately after the forward current flow. Curve (c) in Fig. 3 shows the capacitance variation for the sample that had been kept in hydrogen gas for 2500 min after the forward current flow.

We first examine the variation in capacitance for conventional dehydrogenation. As shown in curve (a) in Fig. 3, the capacitance of the sample exposed to air decreases with time. This is characterized by three different regions. When the hydrogenated sample is exposed to air, hydrogen in the Pd film and at the interface diffuses towards the Pd film

surface to combine with oxygen adatoms on the Pd surface to form water vapor.[3,7] This represents the dehydrogenation of the hydrogenated Pd/GaAs Schottky interface. Because of the removal of the hydrogen at the interface in the dehydrogenation process, the hydrogenation effect, i.e., the hydrogen-induced positive charge at the interface, thus decreases quickly and this causes a decrease in capacitance. The first region thus clearly indicates a removal of hydrogen from the interface. Then, there follows a retardation region in the decrease of capacitance, which is found to be highly dependent to the aging of the sample. For fresh samples, there was no such retardation region.[4] The retardation region is probably due to a poisoned surface[3] caused by usual contaminants such as carbon and sulfur[20] on the Pd film surface. We observed that the time scale for the retardation in dehydrogenation in air could change largely, depending on the aging of the sample. Therefore, by blocking the chemical adsorption sites of hydrogen on the surface[18] it was possible that surface contaminants could retard the dehydrogenation process. After the retardation region, the third region of capacitance change is observed, which behaves similarly to the first one, i.e., the capacitance decreases quickly compared to that in the retardation region.

For the sample that experienced forward current flow followed by immediate exposure to air, there are also three characteristic regions for the capacitance variation as shown in curve (b) in Fig. 3. The first and the third regions of the capacitance variation are similar to those of the conventional dehydrogenation shown in curve (a), except for a much smaller starting capacitance value. In contrast to the slow decrease in capacitance in the retardation region seen in the conventional dehydrogenation shown in curve (a), there appears in curve (b) a remarkable increase in capacitance. Magnification of the peak structure in curve (b) is shown as an insert in Fig. 3. The broad peak for the capacitance covering $\sim$600 min seen in curve (b) corresponds to an increase in the positive charge at the interface (Pd side), which indicates a ''recovery'' of the hydrogenation effect which had been reduced by the forward current flow. It is possible that when hydrogen withdraws from the interface, the hydrogen-related electron traps decompose. This decomposition results in the observed recovery of the hydrogenation effect shown as the broad peak seen in curve (b).

The result in curve (b) in Fig. 3 is considered as a strong evidence that electron traps are closely associated with the hydrogen that is at the interface or has entered the native oxide layer. After exposure of the sample to air so as to drive the hydrogen out of the Pd film through the formation of water vapor on the film surface, the hydrogen that involved in the electron trap diffuses back to Pd film. When the hydrogen reaches the Pd side of the Pd-oxide interface, it forms a hydrogenation-induced dipole once again. The broad peak seen in curve (b) is responsible to this ''rebuilt'' dipole process and is thus considered evidence of decomposition of the electron traps.

Curve (c) in Fig. 3 shows capacitance variation in the dehydrogenation for the hydrogenated sample kept in hydrogen gas for 2500 min after forward current flow (i.e., the same sample used for Fig. 2). One can see that the capacitance variation is quite similar to that of the conventional dehydrogenation and there is only a faint increase of capacitance occurs during the retardation region. This experimental result indicates that the decomposition of the hydrogen-related electron traps had already begun even in hydrogen gas at room temperature after forward current flow.

From the above experimental observation, we speculate that structure changes at the hydrogenated Pd/GaAs interface may occur by the displacement of hydrogen into the native oxide layer which is probably caused by the action of forward current flow. If we assume that the hydrogen at the interface acts as a proton, then the electric field, which is produced at the interface as a result of the applied forward bias, will force the hydrogen to be displaced into the oxide layer. The hydrogen displaced into the native oxide layer would not travel through the native oxide layer because of oxygen in the native oxide which may interact with the hydrogen to form complexes and capture electrons from the forward current flow through the interface. This negatively charged complex thus cancels the effective positive charge formed at the interface by the hydrogenation, and this explains the remarkable decrease of the capacitance shown in Fig. 1 after the forward current flow. When such system is exposed to air, the hydrogen in Pd film and at the interface will diffuse to the Pd film surface to form water with oxygen adatoms on the surface, and this should result in a decrease in the capacitance. However, an increase of the capacitance was observed as a broad peak in curve (b). Because of this, we consider that the hydrogen displaced in the native oxide probably diffused back to the Pd film, resulting in decomposition of the hydrogen-related electron traps. Once it entered in the Pd film at the interface, the hydrogen could result in a dipole with Pd at the interface, similar to that in the hydrogenation process.

The model of electron trap formation described above also successfully explains why the application of reverse biases to the interface did not change the hydrogenation effect: the hydrogen will not be displaced into the oxide layer because of the direction of the electric field.

We have demonstrated that the hydrogen at hydrogenated Pd/oxide interface is active to a large forward current flow and it probably displaced into the oxide to form electron traps. In fact, there is evidence for the reaction between hydrogen and oxygen in many systems. It has been recently reported that the impact of hydrogen on oxygen-covered Ni(100) surfaces produces water at temperatures between 120 and 400 K.[21] There are reports of charge transfer involving the hydrogen adsorbed on the oxide surface.[22–25] Evidence for the interaction of electrons and hydrogen comes from the observation of the formation of negatively charged hydrogen from positively charged hydrogen colliding on oxygen covered surface.[22] Theoretical studies of adsorption of hydrogen on oxide surfaces indicate charge transfer between the surface oxygen atom and the adsorbed proton.[23–25] It is believed that dissociation of hydrogen gas through transition metals results in highly active atomic hydrogen species that react selectively with oxygen atom on the supporting

oxide surface.[26] Some interface states induced at Si/SiO_2 systems have also been attributed to the presence of hydrogen at the interface.[9–12]

IV. CONCLUSIONS

By applying a large forward current (e.g, 0.77 A/cm^2) through a hydrogenated Pd/GaAs interface containing a native oxide, we observed a remarkable reduction in the hydrogen-induced charge at the interface. This observation indicates that the hydrogen at the interface of Pd and GaAs native oxide is active and could be driven into the oxide layer to form electron traps by a forward bias/current applied to the interface. While exposed to air, the Pd/GaAs interface showed an increase in the hydrogen-induced charge during the removal of the hydrogen from the sample; without the effects of a forward current flow a direct decrease in the hydrogen-induced charge would have resulted. This increase in capacitance during the dehydrogenation is considered to be due to the decomposition of the hydrogen-related electron traps. This decomposition resulted from the diffusion of the hydrogen displaced in the oxide back to the Pd side of the Pd/oxide interface to rebuild the dipole as in the hydrogenation. It is clear from our experiment results that both the presence of positively charged hydrogen (proton) at the interface and a sufficient forward bias applied to the interface, which results in electron flow from the semiconductor conduction band, are essential to the formation of hydrogen-related electron traps near the interface.

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