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Apparent Recovery Effect of Hydrogenated Pd-on-GaAs (n-Type) Schottky Interface by Forward Current at Low Temperature*

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The hydrogen-induced charge in the hydrogenated Pd-on-GaAs (n-type) Schottky interface was observed to diminish upon application of forward current at low temperature. This apparent recovery disappears when the sample is heated towards room temperature, that is, the hydrogen-induced charge is reobserved without additional hydrogenation. Thus, it is conceivable that this apparent recovery effect is not due to the removal of the hydrogen, but to variation of the charge state of the hydrogen due to the trapping of the electrons.

KEYWORDS: hydrogen-induced charge, dehydrogenation, forward current, apparent recovery effect, electron trapping

1. Introduction

We have previously reported the change in the electrical characteristics of a Pd-on-GaAs Schottky interface with a native oxide upon exposure to hydrogen ambient (hydrogenation effect).[1)] Hydrogen diffuses through the Pd film resulting in an accumulation of hydrogen at the Pd/oxide interface.[2)] This accumulation induces, in turn, effective electrical charges[3)] at the Pd/oxide interface which decrease[2)] the effective work function of Pd. Thus, hydrogenation causes a variation in the barrier height of the Pd-on-GaAs Schottky interface, i.e., a decrease for n-type (or an increase for p-type) GaAs.[1)] In the previous paper, we also reported that an oxide layer is necessary, to prevent Pd and GaAs from alloying, for the hydrogenation effect to be observed.

A complete recovery of the barrier height to its initial (i.e., before hydrogenation) value is observed by exposing the sample to an oxidizing ambient.[1)] This effect is called dehydrogenation and is explained as follows. The hydrogen in the sample leaves the Pd film surface in the form of water vapor upon exposure to an oxidizing ambient. This removal of hydrogen from the sample thus causes the charge state at the interface to recover to the initial state. The barrier height is then observed to return to the initial value.

We here report a new forward current effect at low temperature in the hydrogenated Pd-on-GaAs (n-type) Schottky interface. By applying forward current through the hydrogenated sample at low temperature, a partial recovery of barrier height variation induced by hydrogenation is observed. This recovery effect, however, disappears when the temperature of the sample is elevated towards room temperature.

Because the capacitance or barrier height variation in the hydrogenated Pd-on-GaAs Schottky interface is due to the presence of hydrogen that is positively charged at the interface, we relate the recovery effect due to the current to the charge state variation rather than hydrogen removal. The dehydrogenation, as described above, is due to the removal of the hydrogen from the sample. We will clarify that the recovery effect due to the current is not a result of the dehydrogenation but of the variation in the electronic charge state.

2. Experimental

An n-type GaAs was used to fabricate the Pd-on-GaAs Schottky interface. A p-type GaAs was also used to confirm the effect of electrons in comparison to holes. The crystal was prepared by vapor phase epitaxy (VPE) on a (100) GaAs substrate. The electron concentration of the VPE layer was 2×10^{15} cm^{-3}. The details of the preparation of the Pd dots on GaAs and their evaluation are reported elsewhere.[1)] In this letter, we only show the data on zero-bias capacitance which is related to the barrier height.

The zero-bias capacitance of the sample was monitored with a 1-MHz capacitance meter (HP 4280A). After hydrogenation by means of exposing the sample to 1 atm hydrogen at room temperature for 30 min, the gas was pumped out below 10^{-6} Torr. The temperature of the sample was controlled between room temperature and 4.2 K in a cryostat (Oxford CF104).

At a desired temperature, a forward current was passed through the sample for a certain length of time. Then we measured the zero-bias capacitance during the cycle of cooling and heating, without breaking the vacuum, in order to confirm the phenomenon at low temperature.

3. Results

Variations of the capacitance for virgin and hydrogenated samples are shown in Fig. 1. Also shown are the capacitances at the initial (C_{ini}) and hydrogenated (C_{hydro}) states. In the virgin sample, the capacitance varies slightly with temperature (curve A* or B*). The variation is slightly greater in the hydrogenated sample (curve A or B). In both cases, no hysteresis was observed.

Marked difference between the two is observed when a forward current of 0.77 A/cm^2 flows for 15 min at low temperature (=77 K, in this case). In the hydrogenated sample, a considerable decrease is observed (curve C), after which the increasing temperature (10 K/min) brings the capacitance back to its hydrogenated value (C_{hydro}) (curve D). The cycle is repeatable, i.e., without

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*This work was performed at the University of Tsukuba.

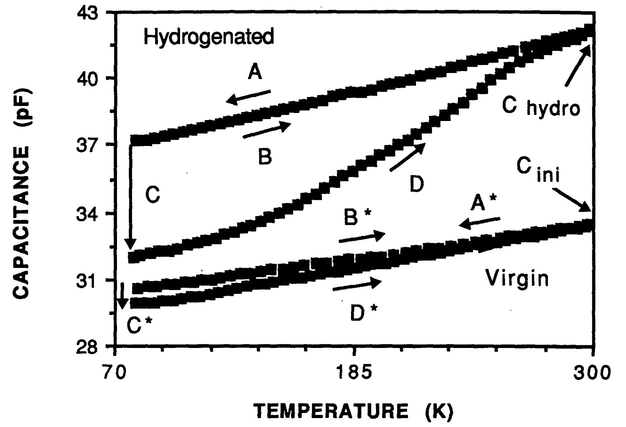

Fig. 1. The zero-bias capacitance of the sample hydrogenated at room temperature was monitored upon (A) cooling, (B) heating without current flow, (C) with flowing forward current of 0.77 mA/cm^2 for 15 min and (D) heating after the current flow. Letters with asterisk (*) are for the virgin sample.

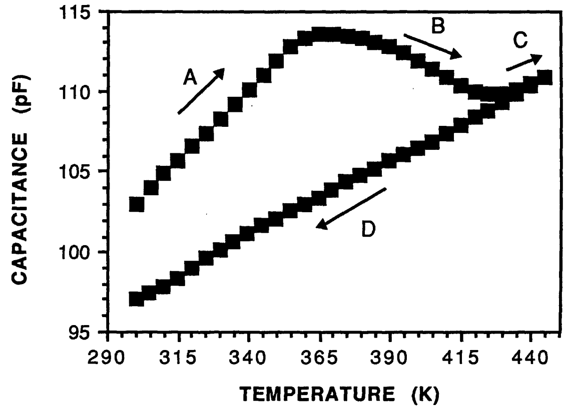

Fig. 2. Change in the capacitance of a hydrogenated Pd-on-GaAs Schottky interface in a heating/cooling cycle between room temperature and 444 K. The capacitance changes with temperature, as indicated by Curve (A) room temperature-370 K, (B) 370–425 K, (C) above 425 K and (D) cooling to room temperature.

current, curves A and B are traced, and with current, hysteresis of A→C→D is traced. In comparison, in the virgin sample, the effect is barely observable. It is confirmed that the apparent recovery (curve C) at low temperature disappears towards room temperature (Curve D), and the sample retains its "hydrogenated" state, thereafter.

4. Discussions

To understand the apparent recovery effect at low temperature due to the current and in comparison to the dehydrogenation effect, we first describe the hydrogenation and dehydrogenation effects. When a sample is exposed to the hydrogen gas ambient, hydrogen atoms diffuse through the Pd film to induce effective charges at the interface, resulting in a reduction of the work function of Pd at the interface.[2] This hydrogenation effect is observed by measuring the electrical characteristics of the Schottky interface.[1] The hydrogen-induced charges at the interface can be reduced by exposing the sample to an oxidizing ambient.[1] Thus, the hydrogenation/dehydrogenation effect is simply due to the accumulation/removal of the hydrogen at the interface.

The dehydrogenation effect is also observed when heating the hydrogenated sample in vacuum well above room temperature. Figure 2 shows a change in the capacitance of a hydrogenated Pd-on-GaAs Schottky interface in a heating (4 K/min) and cooling cycle between room temperature and 444 K. The substrate used was (100) GaAs with an electron concentration of 10^{17} cm^{-3} prepared by the liquid-encapsulated Czochralski (LEC) method. The capacitance increases with temperature in a conventional fashion (i.e., similar to a Schottky interface without hydrogenation) below (Curve A), but starts to decrease above (Curve B) 370 K. At temperatures above a certain level (=425 K, in this case), the capacitance again increases with temperature in a coventional fashion (Curve C). Then the capacitance decreases in a conventional fashion with cooling (Curve D). During cooling to room temperature, the barrier height was seen to recover to the initial value. Two experiments of (1) heating/cooling the sample again showed results for both heating and cooling identical to Curve D in Fig. 2, and (2) repeating hydrogenation followed by the heating/cooling cycle showed results identical to Fig. 2, indicating that no hydrogen remained in the sample. Therefore, we conclude that the removal of the hydrogen from the sample occurs above 350 K. The decrease of the capacitance with increasing temperature between 370 and 425 K (Curve B) is due to the increase of the barrier height. The hydrogen leaves the Pd film in the form of hydrogen gas in the case of heating.[4]

When a forward current flows through the hydrogenated sample at low temperature the capacitance shows an apparent recovery of the hydrogen-induced charges at the interface (curve C in Fig. 1). However, this apparent recovery effect due to the current disappears at room temperature (curve D in Fig. 1) where the hydrogen-induced charges are observed again. This behavior of the capacitance indicates that the nature of the observed recovery effect due to the current is different from that of the dehydrogenation effect. The recovery effect due to the current was also observed at higher temperature, but it did not disappear completely when increasing the temperature, indicating that other effects related to the temperature at which current flows are in play. In order to understand the true mechanism of the recovery effect, we only treat the data at a temperature where the process under flowing current is controlled by just one effect. Complicated cases observed at the higher temperature will be reported elsewhere.

One must note that the sample is kept in vacuum and resupplementary hydrogen is not present. If the hydrogen in the sample moves out of the sample, it cannot return into the sample anymore. The apparent recovery effect caused by current at low temperature is, therefore, not attributable to the removal of the hydrogen from the hydrogenated Pd-on-GaAs Schottky interface but simply to the change in the charge state of hydrogen. Here we discuss a possible model for this apparent recovery effect due to the current.

The hydrogenation effect is due to the effective charges induced by the hydrogen at the Pd/oxide interface. The dehydrogenation effect is due to the removal of such hydrogen from the sample. For the charge state in the Schottky interface to be modified, the hydrogen which induces effective charges must be present at the interface. If the hydrogen is at the interface but does not induce effective charges, it will not modify the charge state at the interface. When a forward current flows through the sample, electrons from the conduction band of GaAs are emitted to Pd through the interface. We thus consider that the observed recovery effect due to the current at low temperature (curve C in Fig. 1) is due to the trapped electrons at the interface, which decrease the hydrogen-induced effective charge density. This model, therefore, does not require the removal of the hydrogen from the interface. This model is schematically illustrated in Fig. 3, in which the energy levels of conduction and valence bands in GaAs as well as the Fermi level are shown. Also shown are the hydrogen-induced charge states at the interface. The hydrogen-induced charge states are qualitatively shown as positive H^+ and neutral H^0, respectively, before (on the left) and after (on the right) a forward current flows through the Pd-on-GaAs Schottky interface. The barrier height ϕ_B is shown to change with the hydrogen-induced charge state.

It is electrons that are trapped, because the recovery effect due to the current is not observed in the p-type GaAs sample. Also important to note in Fig. 1 is that the current effect is marked (curve C in Fig. 1) in the hydrogenated Schottky interface, but it is negligibly small (curve C* in Fig. 1) in the virgin Schottky interface (not exposed to hydrogen). It follows that the electron trap is related to hydrogen. The small current effect in the virgin sample is due to the charge-up effect occurring in the oxide and will be discussed later.

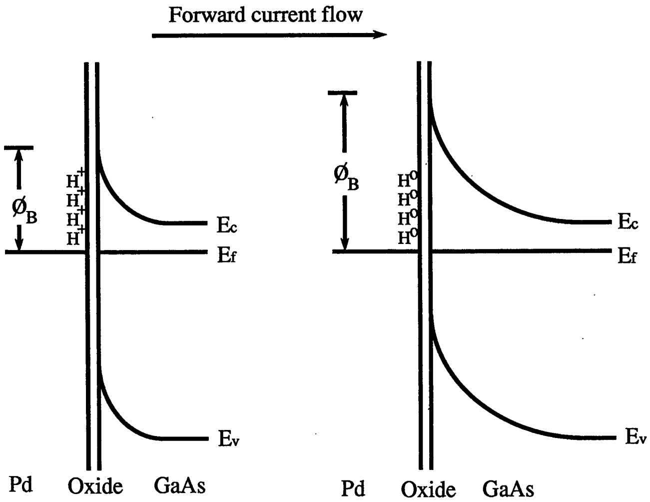

Fig. 3. Schematic hydrogen-induced charge states and energy diagrams showing the barrier heights ϕ_B before (on the left) and after (on the right) a forward current flow.

With this electron trapping taken into consideration, the observed recovery effect due to the current (curve C in Fig. 1) is thought to be due to the reduction of the hydrogen-induced charges. The reduction results from a trapping of electrons from GaAs (Fig. 3). The disappearance of the observed recovery effect upon increasing the temperature of the sample (curve D in Fig. 1) can be explained as the thermal detrapping of the trapped electrons.

We also note that the recovery effect due to the current observed in the hydrogenated Schottky interface is different from a simple charge-up effect already observed in the oxide layer. It is reported that forward current flow changes the trap density in the oxide of the metal/SiO_2/Si system.[5] Current flow is also found to create defect states in a thin SiO_2 layer[6] and hydrogenated amorphous silicon.[7] Recently, it has been reported that a forward current causes a charge-up which changes the barrier height of a metal/GaAs Schottky interface with a thin oxide layer.[8,9]

We also observed this kind of charge-up effect in our virgin Pd-on-GaAs Schottky interfaces. The decrease of the capacitance (curve C* in Fig. 1) shows the charge-up effect when forward current flows through the interface; the charge-up effect occurred in the oxide layer. This is proven by measuring oxide-free Schottky interfaces prepared by annealing or by depositing Pd on the $(NH_4)_2S_x$-treated GaAs surface. These treatments promote the reaction of Pd and GaAs, resulting in interfaces without oxygen.[1] The observation of the charge-up effect on the virgin Pd-on-GaAs Schottky interface (curve C* in Fig. 1) is consistent with the reported results.[5,8,10]

The Pd-on-GaAs Schottky interface is interesting because the local charge at the interface can be modified by atomic hydrogen. Charge redistribution at the interface plays an important role in the determination of the barrier height of a Schottky interface.[11] In our experiment on the Pd-on-GaAs Schottky interface we clearly show that the charge state modified by hydrogen is also changed by electrons from GaAs. In a Schottky interface with metals such as Al, Ag and Au, the charge state at the interface is difficult to change. Therefore, the Pd-on-GaAs Schottky interface with hydrogen, as an effective probe of the charge state at the interface, is a useful system for exploring the nature of the interface.

5. Conclusions

We studied the newly found apparent recovery effect due to a forward current at low temperature flowing through the hydrogenated Pd-on-GaAs Schottky interface. However, this apparent recovery effect due to the current is not due to the removal of the hydrogen at the interface, but to a reduction of the effective charge induced by the hydrogen. A hydrogen-related trap center model is described to explain the apparent recovery effect at a low temperature and its disappearance at a higher temperature. We emphasize that the effect observed in our experiment is of importance in exploring the behavior of hydrogen and local charge redistribution at the metal-semiconductor interface. However, the origins of the trap centers remain to be clarified.

Acknowledgment

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