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Pd-on-GaAs Schottky Contact: Its Barrier Height and Response to Hydrogen

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A Pd-on-GaAs Schottky contact was prepared by depositing palladium using a tungsten heater, rather than electron-beam heating, onto a GaAs surface. The interface composition was investigated by sputter Auger electron spectroscopy. An intermediate layer resulting from the reaction of Pd and GaAs was observed under certain conditions. The Schottky barrier height estimated from the measurements of forward current-voltage (*I-V*) or reverse capacitance-voltage (*C-V*) characteristics was found to depend on the interface structure. The response of the Schottky contact to hydrogen was found to be correlated with the barrier height. We pointed out that hydrogen can be used as a probe to the interface structure, whether metallic Pd or an intermediate material of Pd–Ga–As is in contact with GaAs. The observation was consistent with both p- and n-type GaAs.

KEYWORDS: Pd-on-GaAs, Schottky contact, work function, barrier height, reaction at interface, hydrogenation, variation of barrier height

§1. Introduction

The formation mechanism of metal/GaAs contact has been studied for several decades, but is not yet completely understood. The observed value of the barrier height of the contact does not follow a simple theory in terms of the metal work function and the electron affinity of GaAs. Many models[1-6] have been developed to explain the discrepancy. Among them, the effective work function model[3] proposed by Freeouf and Woodall emphasizes the role of the intermediate layer formed by the reaction[4,5] between the metal and GaAs to determine the barrier height. The Schottky limit[7] of 1.05 eV is simply calculated for a Pd/GaAs Schottky contact with a Pd work function of 5.12 eV[8] and GaAs electron affinity of 4.07 eV.[9] Values[10-13] estimated from capacitance-voltage (*C-V*) measurements scatter between 0.88 and 0.97 eV, and the discrepancy might be attributed to the intermediate layer.

Structures of the interfaces[14-19] of Pd on GaAs have been reported in the light of the reaction of Pd with GaAs. It is observed that Pd occasionally penetrated the native oxide layer on GaAs even at room temperature, especially when electron beam deposition of Pd was employed.[14,15,19] It is reported that an interface structure of Pd/Pd–Ga–As/GaAs is formed which may determine the barrier height of the Pd-on-GaAs system.[14] In this case, it is obvious that an ideal Pd/GaAs interface is anything but realized.

On the other hand, reports on electrical characteristics of Pd/GaAs Schottky contacts are scarce.[10-13] More importantly, there has been little study done in order to relate the irreproducible electrical characteristics of Pd-on-GaAs Schottky barriers to the above-mentioned metallurgical interface.

Hydrogen is known to dissolve into Pt-group metals, and the atomic hydrogen has an unusually high diffusion coefficient, especially in Pd.[20] It has been reported that the electrical characteristics of a Pd/SiO_2/Si diode are affected by hydrogen.[21-23] The effect is attributed to the formation of electrical dipoles at the metal-oxide interface. The dipole is believed to result from the s-type adsorption of hydrogen atoms inside the Pd film at about 0.5 Å from the interface.[22]

Aspnes and Heller[11] have reported on a hydrogenation experiment on GaAs Schottky contacts of Ru, Rh, Ir, Os, Pd, and Pt. With Ru, Rh, and Ir, the Schottky barriers responded to hydrogen. With Os, they observed a faint response, but failed to acquire data due to the poor contact. With Pd and Pt, the barriers showed no response. They suggested that the interface structure might be responsible for the different behaviors.

There has been no report, as far as the present authors know, on the Pd/GaAs Schottky contact which responded to hydrogen. We found that, in some Pd-on-GaAs contacts, the electrical characteristics are affected by hydrogen.

In this study, we clarified the relation between the structure in Pd-on-GaAs Schottky contacts and their electrical characteristics, as well as their responses to hydrogen. The interface structure was observed by sputter Auger electron spectroscopy (AES) and the barrier height of the contact was evaluated by current-voltage (*I-V*) and *C-V* measurements. We report here that the native oxide layer makes the difference of Pd-on-GaAs interfaces in two aspects, the barrier height and its response to hydrogen.

§2. Experimental

The substrates used in this study were (100) n- and p-type GaAs. N-type GaAs is prepared by the liquid encapsulated Czochralski (LEC) method and p-type GaAs by the horizontal Bridgman (HB) method. The dopant in n-GaAs is Si, and Zn in p-GaAs. The carrier concentration of the substrate was estimated from *C-V* measurements as 1×10^{17} cm^{-3} for n-type and 6×10^{16} cm^{-3} for p-type GaAs.

The ohmic contact was formed by wetting the back side of the wafer with indium and heating it in H_2 ambient at 400°C for 5 min. Subsequently, a thin film of Au was deposited so as to protect indium from chemical reaction during the following process.

Before setting the substrate in an evaporation chamber

provided with an ion pump, a cleaning process was performed as follows. The substrate was first ultrasonically degreased in trichloroethylene, acetone and methanol, sequentially. Then, the substrate was rinsed in deionized water and blown with N_2 gas. Finally, the substrate was etched in a 5:1:1 H_2SO_4:H_2O_2:H_2O solution at 60°C for 2 min followed by a rinse in deionized water for 5 min. Immediately, the substrate was dried by N_2 gas and set in the evaporation chamber. A native oxide layer is formed on the substrate prepared in the manner mentioned above.[24] The substrate thus prepared is hereafter called a "chemically etched" substrate.

For the sake of comparison, a substrate without a native oxide layer was also prepared. The substrate was dipped in $(NH_4)_2S_x$ solution[25] at 60°C for 5 hours, then set into the chamber after blowing with N_2 gas. It is known that the thus-prepared surface is free from oxygen or oxide but is covered with an atomic layer of sulfur.[26]

A metal mask with 500-μm-diameter holes was used for making Schottky contact dots. Palladium was deposited onto the substrates by heating the tungsten heater wound with a 0.5ϕ palladium wire attached in a pressure on the order of 10^{-7} Torr or less. The tungsten wire was placed about 25 cm below the mask. The deposition rate was about 3 Å/s, and the thickness of Pd films was 120–180 Å.

The interface composition was investigated by sputter AES. The AES data were obtained using 10 keV incident electrons. An argon ion beam with energy of 3 keV was used to observe the depth profile. Peaks at 330 eV for Pd, 503 eV for O, 152 eV for S, 1070 eV for Ga and 1229 eV for As were used to mark the elements, respectively.

The *I-V* and *C-V* measurements were performed using a sensitive electrometer (Advantest TR8652) with a built-in voltage source and a 1-MHz capacitance meter (HP 4280A), respectively.

The *I-V* and *C-V* characteristics of chemically etched specimens were measured at room temperature. The effect of isochronal (15 min) annealing was measured on specimens from the same wafer. The *I-V* measurements were performed in the forward voltage range of between 0 and 0.6 V, and *C-V* measurements in the reverse voltage range to −2 V. The measurement was done in air, vacuum and H_2 ambient. From these data, barrier heights of Pd-on-GaAs Schottky contacts were derived.[27] In order to confirm the uniformity of the Schottky contacts on a substrate, at least three dots were measured. Usually, the scattering of the data was minimal.

The measuring chamber was pumped out with rotary and oil diffusion pumps. After a pressure on the order of 10^{-4} Torr was obtained, the pumps were cut off, and H_2 gas was introduced up to 0.5 atm. In the hydrogenation process, the zero-bias capacitance of the Schottky contact was monitored with the 1-MHz capacitance meter. When stabilized, *C-V* and *I-V* measurements in H_2 ambient were taken in order to determine the barrier height. Then, the chamber was pumped out again to purge the H_2 ambient, and air was introduced to observe the dehydrogenation process, the change in the zero-bias capacitance to the initial state.

§3. Results

3.1 *Interface structure and barrier height*

We analyzed the surface/interface by means of sputter AES. Data are shown in Fig. 1 for a chemically etched specimen at the three different states of (a) as prepared and (b) after heating at 150°C and (c) at 250°C. The chemically etched sample (Fig. 1(a)) had the most abrupt interface. The sulfur signal noted at the surface is due to the contamination of the vacuum chamber caused by the sulfur-involving experiment in our laboratory. We confirmed that the results of the heat treatment at high temperatures in H_2 flow were basically identical to those in Ar flow. At low temperatures, however, the reaction of Pd and GaAs was much easier in the former ambient. In order to form a reacted interface by the heat treatment, therefore, the sample was annealed in H_2 flow. After annealing the sample in a quartz furnace at 150°C for 15 min in H_2 flow, a weak intermixing of Pd and GaAs at the interface is observed, as in Fig. 1(b). To completely consume the metallic Pd, an annealing at 250°C was also performed. Depth profiles by sputter AES in Fig. 1(c) show the complete reaction of Pd and GaAs, forming the intermediate layer of Pd–Ga–As. It has been found that the dominant mobile element in a Pd-on-GaAs system is Pd.[19] We thus interpreted the result shown in Fig. 1(c) to be the complete penetration of Pd into the substrate.

Recently, Sands *et al.*[14,19] reported on the reaction in a Pd-on-GaAs system and concluded that Pd penetrated the native oxide layer during room-temperature deposition to react with GaAs, forming a ternary phase of Pd–Ga–As. They called this state "phase I", which dominates up to 250°C.[14,19] Thus, the mixed region in Fig. 1(c) corresponds to this phase I.

In the case of chemically etched samples before (Fig. 1(a)) and after annealing at 150°C (Fig. 1(b)), the formation of phase I is not clearly observed. Considering that the reaction at the interface will bring some variations on the electrical characteristics of the Schottky contact, forward bias *I-V* and reverse bias *C-V* data were measured.

The saturation current density J_s can be estimated in the *I-V* curve on a semilogarithmic graph, from the extrapolated intercept with the ordinate. Barrier height ϕ_b is then derived from the equation[27]

$$\phi_b = kT \ln (A^{**}T^2/J_s), \tag{1}$$

where k is Boltzmann's constant, T the absolute temperature, and A^{**} is the effective Richardson constant of 8.16 and 74.4 A cm^{-2}K^{-2} for n-type and p-type GaAs, respectively.

Figure 2(A) shows typical *I-V* data for the chemically etched sample (n-GaAs). The barrier height ϕ_b of the sample was estimated as 0.95 eV by using eq. (1). The ideality factor (n-value) is obtained from the slope of the *I-V* curve and was estimated as 1.09. The Schottky junction in Fig. 2(A) is characterized by the barrier height and ideality factor as 0.95 eV/1.09. The reproducibility of the data within the same batch was usually good, but we found that the barrier heights for specimens from different batches scattered in the range from 0.85 eV/1.05 to 0.98 eV/1.17. We will discuss this distribu-

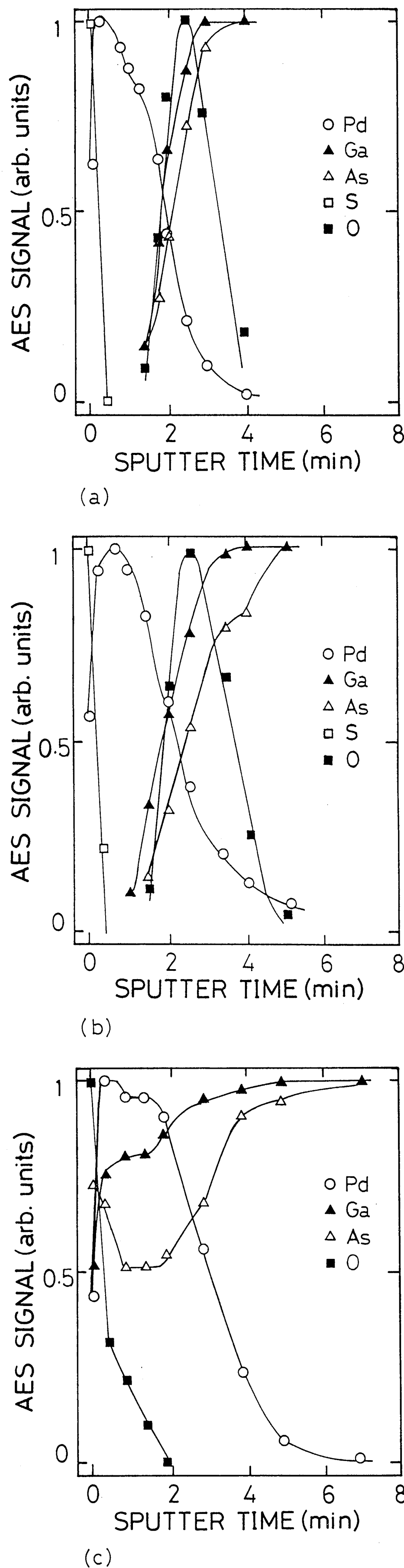


Fig. 1. Depth profiles by sputter AES for Pd-on-GaAs interfaces: (a) as prepared and (b) after heating in H_2 ambient for 15 min at 150°C and (c) at 250°C. The sample is prepared by depositing Pd on a chemically etched GaAs surface.

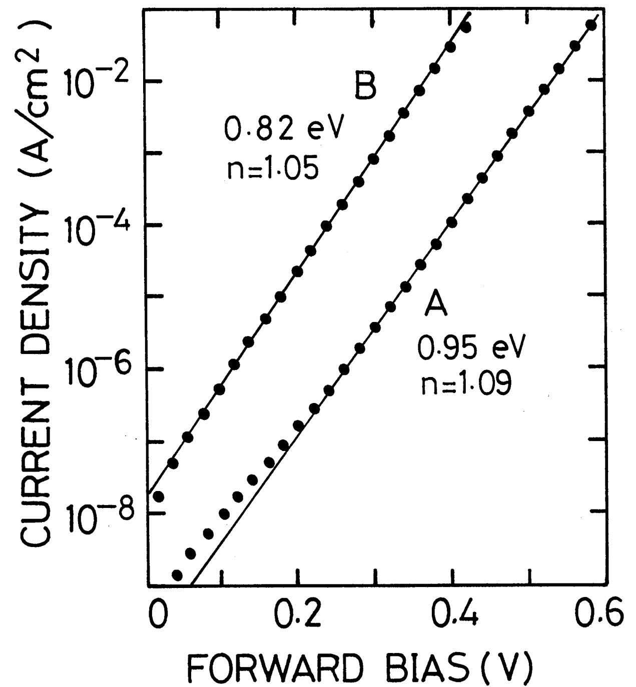


Fig. 2. Typical forward *I-V* data of the chemically etched Pd-on-GaAs Schottky contacts for (A) before heating, and (B) after heating in H_2 ambient for 15 min at 150 or 250°C, respectively. The interface structure for a Schottky barrier with *I-V* curve A is shown in Fig. 1(a) and those with curve B are Figs. 1 (b) or 1(c), respectively.

tion of barrier heights in §4.

Figure 2(B) shows the data after 150°C annealing for 15 min. The data were almost unchanged by 250°C annealing. The barrier height/ideality factor was 0.82 eV/1.05. After annealing, the deviation of the estimated barrier heights was minimal.

From *C-V* measurement, the result is drawn as a Mott-Schottky plot of C^{-2} against reverse bias voltage. The plot is expressed by the equation[27]

$$C^{-2}=2(V_{bi}-V)/(N_d\varepsilon_s\varepsilon_0 qA^2), \quad (2)$$

where N_d is the dopant concentration, ε_s the dielectric constant of GaAs, ε_0 the permittivity in vacuum, q the elementary charge and A the Schottky contact area, respectively. V_{bi} is the intercept of the plot with the abscissa, from which barrier height ϕ_b is calculated from the equation[27]

$$\phi_b=qV_{bi}+qV_{n,p}+kT, \quad (3)$$

where $qV_{n,p}$ is the difference of the Fermi level from the conduction or valence band for n- or p-type GaAs, respectively. $qV_{n,p}$ can be calculated from the dopant concentration.

Figure 3(A) shows the *C-V* data for the same chemically etched sample as used in the *I-V* measurement mentioned above, and the estimated barrier height ϕ_b is 1.05 eV. It varied between 0.92 and 1.18 eV in different batches. Figure 3(B) shows the data after annealing at 150 or 250°C. The barrier height is reduced to 0.88 eV with minimal deviation.

Thus, the barrier height in the "as-deposited" state for the chemically etched sample, 0.95 eV (from *I-V* data) or

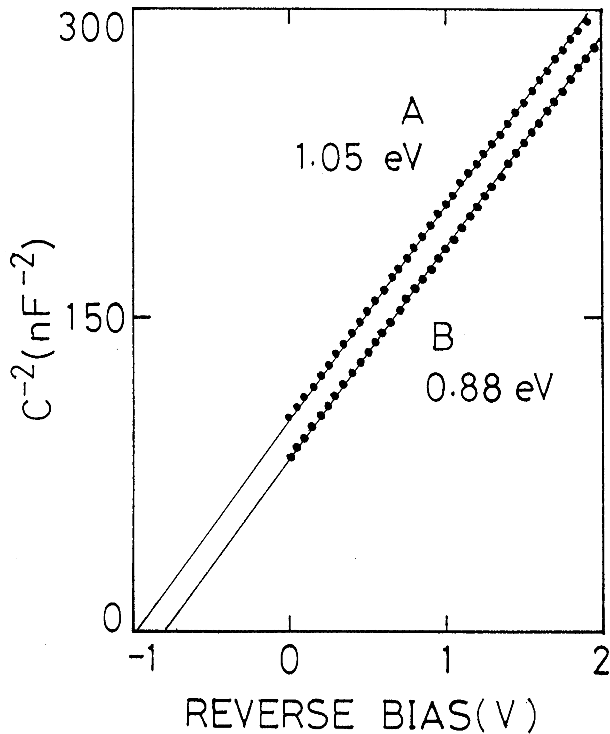


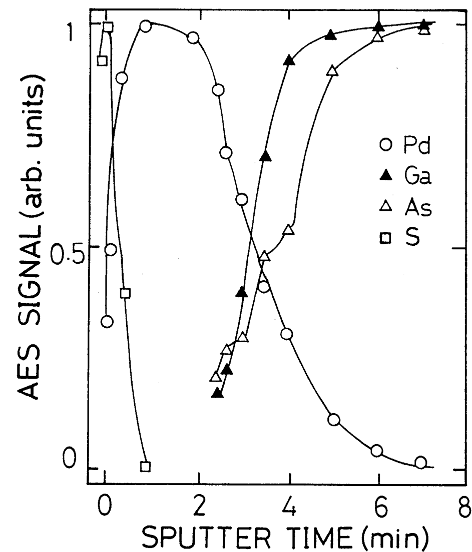
Fig. 3. Reverse *C-V* data at 1 MHz corresponding to those of *I-V* shown in Fig. 2.

1.05 eV (from *C-V* data), is reduced by the heat treatment. The change is obviously caused by the reaction at the interface which forms the phase I interface. Before the heat treatment, the barrier height is affected by the presence of oxygen at the interface, which is seen in Fig. 1. On heating at 150°C, Pd gradually penetrated GaAs, which can hardly be recognized in Fig. 1(b). However, the barrier height is lowered by the formation of the intermediate state, phase I.

The native oxide layer plays a role to hinder or retard the reaction of Pd and GaAs. In the experiment of Sands *et al.*,[14] Pd was evaporated by electron-beam heating, which is known to cause damage to GaAs easily. Actually, the penetration of Pd is observed in the as-deposited interface in their experiment. We evaporated Pd by resistance heating, which assured us of a Schottky barrier height of 1.05 eV higher than the conventionally reported values[10-13] of below 0.97 eV. However, we were also able to prepare a Schottky contact with a low barrier height of 0.92 eV (*C-V*). In this case, phase I is considered to be formed during the evaporation.

On substrates without the native oxide layer, Pd is considered to react easily with GaAs during the room-temperature deposition process. In order to clarify the role of the native oxide in the Pd-on-GaAs system, we turned to an oxygen-free surface, the $(NH_4)_2S_x$-treated surface of GaAs. The sulfide-treated surface is free from oxygen adsorption.[26]

Palladium film was deposited on the $(NH_4)_2S_x$-treated surface in the same way as stated before. The depth profiles by sputter AES are shown in Fig. 4. We did not detect the presence of sulfur at the interface by AES measurement. Remarkable differences noted in Fig. 1 are



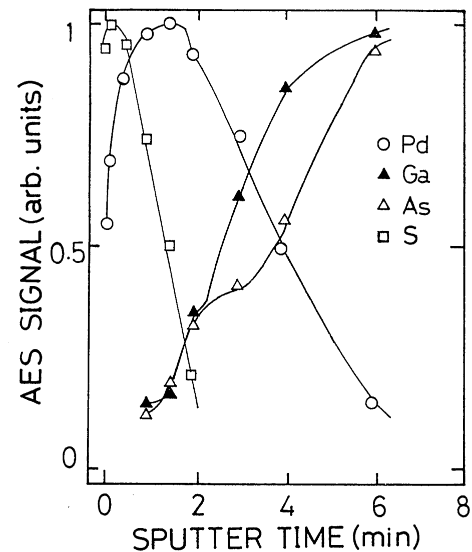


Fig. 4. Depth profiles by sputter AES for Pd-on-GaAs interfaces: (a) as prepared and (b) after heating in H_2 ambient for 15 min at 150°C. The sample is prepared by depositing Pd on a $(NH_4)_2S_x$-treated GaAs surface.

that (1) no oxygen was detected at the interface (Fig. 1(a) vs Fig. 4(a)), and (2) there was faster intermixing of Pd and GaAs by 150°C heat treatment [Fig. 1(b) vs Fig. 4(b)].

The barrier height of the $(NH_4)_2S_x$-treated sample was 0.86 eV/1.05 from *I-V* or 0.91 eV from *C-V* data. This value of the barrier height was almost equal to that of the chemically etched sample in which phase I was accidentally formed, as mentioned above. The barrier height is only slightly modified by heat treatment to 0.82 eV/1.05 (*I-V*) or 0.88 eV (*C-V*). On both the chemically etched surface and the $(NH_4)_2S_x$-treated surface, the barrier heights after annealing are identical, which supports the idea that the intermediate layer of Pd–Ga–As determines the barrier height.

Barrier heights were also measured for p-type GaAs. At room temperature, the chemically etched sample showed an ohmic like contact due to the low barrier height, and *C-V* measurement was not possible. Therefore, the barrier height was not obtainable.

However, the barrier height was obtained in the $(NH_4)_2S_x$-treated sample. It was 0.43 eV/1.20 (*I-V*) or 0.54 eV (*C-V*). Annealing the samples (both chemically etched and $(NH_4)_2S_x$-treated) resulted in a slightly higher barrier height of 0.45 eV/1.20 (*I-V*) or 0.58 eV (*C-V*).

The data of the barrier height at various interface structures are summarized in Table I. We notice that the sum of the barrier heights of n- and p-GaAs is close to the band gap energy of 1.42 eV at room temperature. Particularly, for the annealed and $(NH_4)_2S_x$-treated samples, the sum of the barrier heights (*C-V*) is very close to the value of the band gap energy. This leads us to conclude that the interfaces of Pd on the two types of GaAs are identical. For the chemically etched case, the relationship of the sum and the band gap energy is not so clearly observed. The reason, as we will discuss in §4, is that the Pd-on-GaAs interface structure is uncertain when a native oxide layer is present on the surface of GaAs. However, the trend of the interface structure on the barrier height is clear.

3.2 *Hydrogenation*

In order to clarify the role of the intermediate layer, or phase I, we performed a hydrogenation experiment. Before heat treatment, in samples of the chemically etched surface, the barrier height (n-type GaAs) was lowered by hydrogen. All the other samples in which the intermediate layer was (supposedly) existent were insensitive to hydrogen.

We realize that the hydrogenation/dehydrogenation phenomenon is very complex. Variation of the junction capacitance at zero bias was measured upon hydrogenation (in 0.5 atm H_2 ambient) and dehydrogenation (evacuation followed by exposure to air). We found that the carrier concentration did not vary after hydrogenation or dehydrogenation. Therefore, we presumed the carrier concentration was also unchanged during those processes. As a result, the barrier height during hydrogenation and dehydrogenation was derived by the zero-bias capacitance using eq. (2). In order to make the variation of the barrier height clear, the stabilized barrier height in H_2 ambient was used as the reference.

Temporal response is shown in Fig. 5. Apparently, the hydrogenation is in two steps whose time constants (τ_1 and τ_2) are ~ 3 s and $\sim 3\times10^1$ s, respectively. Dehydrogenation in vacuum is slower than hydrogenation, and the recovery is only partial (at room temperature). A complete recovery is obtained at room temperature in air. However, the recovery time varied widely in the range from a few minutes to a few tens of hours, presumably depending on the surface contamination of the Pd film. Hydrogenation and dehydrogenation were repeatable.

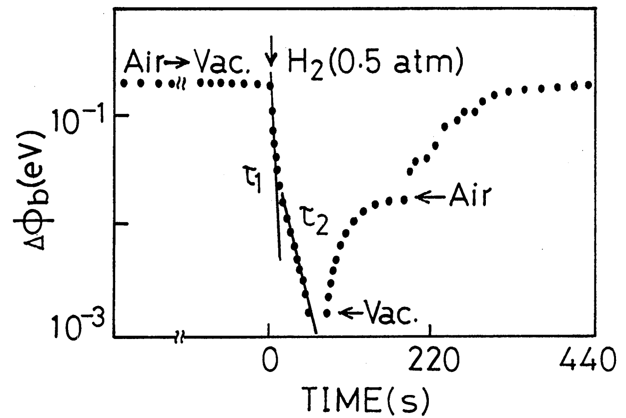


Fig. 5. Hydrogenation and dehydrogenation processes expressed by $\Delta\phi_b$, the barrier height (n-GaAs) referring to the stabilized barrier height in 0.5 atm H_2. The barrier height was derived from zero-bias capacitance.

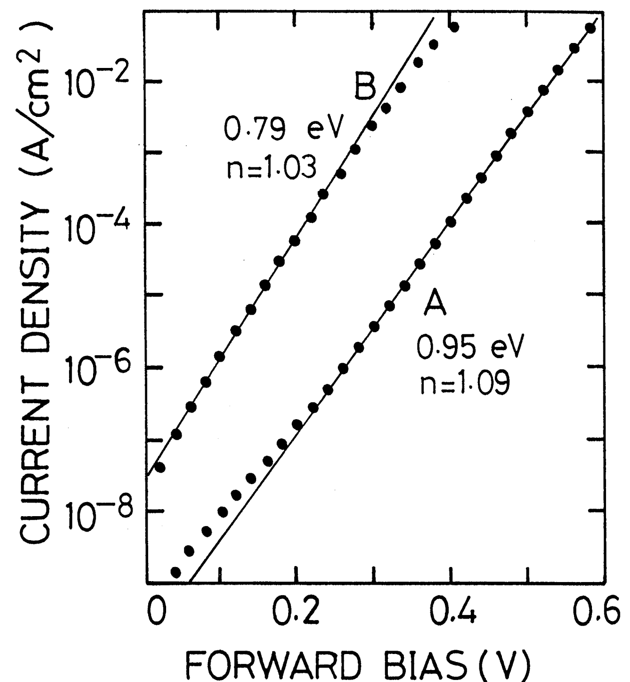


Fig. 6. Forward *I-V* data for a typical chemically etched sample (A) in air (also in vacuum) [the same as shown in Fig. 3(A)] and (B) in 0.5 atm H_2 ambient.

Table I. The barrier height of Pd-on-GaAs Schottky contact under various interface structures. Thermal annealing was done for 15 min in H_2 at 150 or 250°C for chemically etched and 150°C for $(NH_4)_2S_x$-treated cases.

	Chemically etched		$(NH_4)_2S_x$-treated	
	before annealing	after annealing	before annealing	after annealing
n-type GaAs				
$\phi_b^{I\text{-}V}$ (eV)	0.95	0.82	0.85	0.82
$\phi_b^{C\text{-}V}$ (eV)	1.05	0.88	0.91	0.88
n-value	1.09	1.05	1.05	1.05
p-type GaAs				
$\phi_b^{I\text{-}V}$ (eV)	****	0.45	0.43	0.45
$\phi_b^{C\text{-}V}$ (eV)	****	0.58	0.54	0.58
n-value	****	1.20	1.20	1.20

****: Data not available due to low barrier heights.

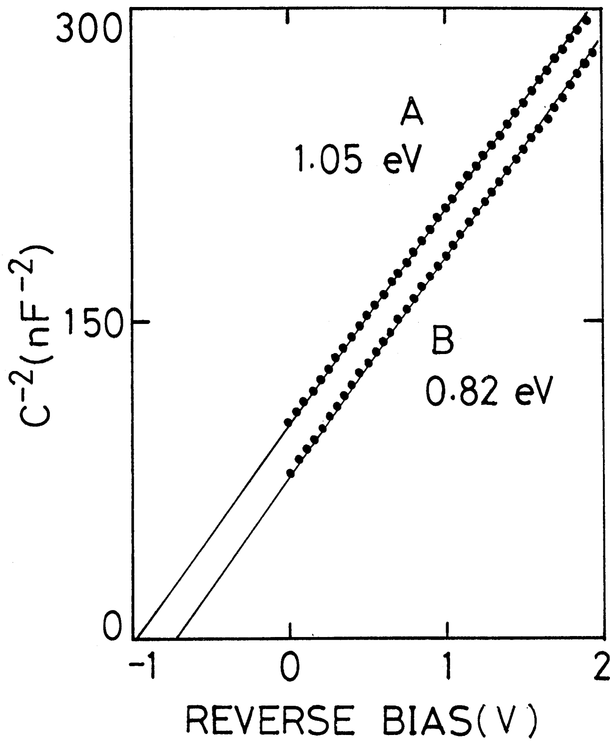


Fig. 7. Reverse *C-V* data at 1 MHz corresponding to those of *I-V* shown in Fig. 6.

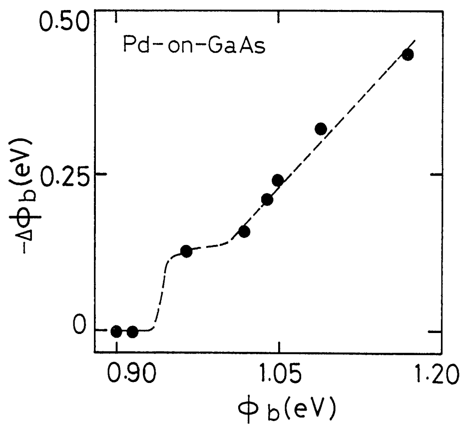


Fig. 8. The sensitivity $\Delta\phi_b$ of the Pd-on-GaAs (n-type) Schottky contact to hydrogen versus the initial value of the barrier height in air. The different barrier heights in air resulted from different batches of Pd deposition on chemically etched GaAs surfaces.

Table II. Variation of the barrier height of a typical chemically etched Pd-on-GaAs Schottky contact (before heating) due to hydrogenation at room temperature.

	Air	H_2 (0.5 atm)
n-type GaAs		
ϕ_b^{I-V} (eV)	0.95	0.79
ϕ_b^{C-V} (eV)	1.05	0.82
n-value	1.09	1.03
p-type GaAs		
ϕ_b^{I-V} (eV)	****	0.50
ϕ_b^{C-V} (eV)	****	0.70
n-value	****	1.20

****: Data not available due to low barrier heights.

In Fig. 6 *I-V* data of the chemically etched sample (A) of the initial state in air (or in vacuum) and (B) after hydrogenation, respectively, are shown. Also shown are *C-V* data in Fig. 7 for the corresponding conditions. Curves A (before annealing) in Figs. 6 and 7 are identical to those in Figs. 2 and 3. The barrier height after hydrogenation is lowered to 0.79 eV/1.03 from *I-V* data (curve B in Fig. 6) or 0.82 eV from *C-V* data (curve B in Fig. 7). We also noted that flowing current across the Schottky barrier brought about an effect similar to dehydrogenation.

Some of the chemically etched samples failed to respond to hydrogen. We found the correlation between the barrier height (n-GaAs) and the sensitivity, the variation of the barrier height due to hydrogenation, to be as shown in Fig. 8. We interpret that this phenomenon is connected to the degree of reaction at the Pd-on-GaAs interface. When the reaction is complete, there is no response.

In the case of p-type GaAs, the barrier heights of some of the chemically etched samples varied in H_2 ambient. The barrier height of a typical sample was observed to increase to 0.50 eV/1.20 (*I-V*) or 0.70 eV (*C-V*) in H_2 ambient. Their response to hydrogen is summarized in Table II.

§4. Discussion

In Table I, it is shown that the barrier height is relevant to the interface structure. In the chemically etched samples, the barrier height varied between 0.92 and 1.18 eV (*C-V*) in different batches. Samples with an intermediate layer, phase I, have lower barrier heights of between 0.88 and 0.91 eV (*C-V*). The latter samples are obtained either by removing the native oxide by means of $(NH_4)_2S_x$ treatment or by annealing at 150–250°C. If we followed the theory of Schottky,[1] from the barrier height (0.88 eV) of the samples in which intermediate layer dominates the interface, the work function of the intermediate material is assumed to be about 0.17 eV lower than that of Pd. However, the value of 0.17 eV must be tested in future work on the intermediate material.

On the chemically etched surface, we were not able to precisely control the native oxide layer. The detailed interface structure of Pd-on-GaAs may be different on every fabrication batch. Pd may be separated from GaAs by the native oxide or it may penetrate through[14,19] the crack of the oxide to form the intermediate layer. For each fabricated batch, however, the barrier heights on one pellet were uniform. Low barrier heights of chemically etched samples are assumed to be due to the intermediate layer, occasionally formed during the room-temperature deposition process. This assumption is supported by the result of Sands *et al.*[14,19] Moreover, our hydrogenation result also gives strong support for intermediate layer formation on the chemically etched surface during the room-temperature deposition process. In this kind of sample, the diode characteristics are good with an ideality factor of 1.05.

Barrier heights taken after annealing converge to a low value of 0.82 (*I-V*) or 0.88 eV (*C-V*), irrelevant of the surface treatment. The conclusion is drawn that the in-

termediate layer, phase I, results in a low barrier height.

Atomic hydrogen in Pd is known to induce a dipole at the Pd/SiO_2 interface of a $Pd/SiO_2/Si$ structure.[21] But, at a reacted interface of Pd/Pd–Ga–As/GaAs, metallic Pd is not in contact with GaAs and an atomic hydrogen-induced dipole may not exist. Even if atomic hydrogen diffuses into the reacted interface, its behavior could be different from that in the Pd film at the unreacted interface. In the present paper, we present an idea clarifying the interface structure: to use atomic hydrogen as a probe to the interface of the Pd-on-GaAs Schottky contact.

Typical data on hydrogenation for the sample with the barrier height of 1.05 eV (*C-V*) is shown in Table II. Only chemically etched samples responded to hydrogen.

The variation of the Schottky barrier height in H_2 ambient is explained in the light of the atomic hydrogen-induced dipole model.[21] Hydrogen gas dissolves into Pd film as atomic hydrogen, then penetrates through the film with a very high diffusion coefficient.[20] At the interface of Pd/oxide/GaAs, atomic hydrogen sees an abrupt boundary of metallic Pd film, where the s-type adsorption[22] occurs. As a result, the surface dipole is induced. The surface dipole lowers the surface work function of Pd.[21] Thus, the reduction of the Pd work function causes the decrease of the barrier height of the Pd-on-GaAs (n-type) Schottky contact. This phenomenon can also be explained by the atomic hydrogen-induced charge at the interface. In fact, we have directly observed charge transfer generating open voltage or current flow during the hydrogenation process.*

The variation in the barrier height by an atomic hydrogen-induced dipole is described. From the experimental data in Table II, we can deduce that the condition for the hydrogenation to be observed is when the intermediate layer is not formed. In other words, it happens when the Pd work function contributes to the determination of the barrier height of the Pd-on-GaAs Schottky contact. Therefore, when the work function is lowered by atomic hydrogen, the barrier height is lowered for n-GaAs, or increased for p-GaAs.

A reacted interface, at which an intermediate layer of Pd–Ga–As is present, must show different electrical behavior from that of the unreacted interface described above. The reaction of Pd and GaAs is enhanced by annealing the chemically etched samples. When the surface is oxygen-free, as in the case of the $(NH_4)_2S_x$ treatment, the reaction takes place as soon as Pd is deposited. The results shown in Table I give a clear demonstration supporting this hypothesis.

At the interface of phase I/GaAs, atomic hydrogen will not act in the same way as in the case when metallic Pd is present at the interface. Our hydrogenation experimental results clearly showed that in the annealed samples, their barrier heights were not modified by exposure to H_2 ambient. This fact showed that even when metallic film remained on the surface (Fig. 1(b)), i.e., even when atomic hydrogen might penetrate into the film, the barrier height was not modified. Therefore, the metallic Pd on the surface does not determine the barrier height, but the intermediate layer of Pd–Ga–As does. It seems that the work function of Pd–Ga–As is not affected by hydrogen. This hydrogenation result strongly supports our interpretation of interface structure on the barrier height.

We also found that the chemically etched samples were not always responsive to hydrogen, and that the sensitivity depended on the barrier height, as shown in Fig. 8. Only samples with barrier heights larger than 0.96–0.99 eV responded to hydrogen, and the sensitivity increased with the increase of the barrier height.

A relatively thick native oxide layer hindered the formation of the phase I due to the nonreactive property of Pd and the oxides of Ga and As.[28] It is reported that for reactive metals, the presence of an adequate thickness of the oxide layer modifies the barrier height to a better fit[29] to the Schottky limit,[7] but if the oxide layer is too thick, it increases[30,31] the barrier height as well as the ideality factor. Therefore, the native oxide layer has two effects for the system of Pd on GaAs: enhancement of the dominance of metallic Pd at the interface and increase of the barrier height and the ideality factor.

The response of the barrier height to hydrogen is with the increase in the degree of dominance of metallic Pd at the interface, which increases the barrier height of the Pd-on-GaAs Schottky contact. Figure 8 shows the variation of the barrier height due to hydrogenation versus the barrier heights (in air). It is interesting to notice that a "critical barrier height" exists in order for the hydrogenation to be observed. Its value is 0.96–0.99 eV (*C-V*). If the barrier height is less than the critical value, the Schottky contact is insensitive to hydrogen.

The interfacial layer has different influences[29,31,32] on the Schottky barrier formation. In this study, we found that the most meaningful effect of the native oxide layer was its hindrance to the reaction of Pd and GaAs. This conclusion is supported by the hydrogenation experimental results. It is reasonable to consider that at the critical value (Fig. 8), Pd/oxide/GaAs switches to Pd/Pd–Ga–As/GaAs at the Pd-on-GaAs interface.

Thus, the results of hydrogenation give us a picture of the dependence of the barrier height on the interface structure in the Pd-on-GaAs system. For the chemically etched samples with barrier heights larger than the "critical barrier height", 0.96–0.99 eV (*C-V*), the barrier height is relevant to the Pd/oxide/GaAs interface, while for those with barrier heights smaller than that, to the phase I/GaAs interface. Aspnes and Heller[11] reported a hydrogenation experimental result for a Pd-on-GaAs Schottky contact (with a barrier height of 0.85 eV which was estimated from *I-V* characteristics) and concluded that atomic hydrogen did not modify the barrier height. Although their sample was a chemically etched one before heating, the value of the low barrier height suggested the formation of a reacted interface, i.e., phase I determined the barrier height. As a result, hydrogen did not modify the Pd-on-GaAs Schottky barrier height in their experiment.

We compare the reported barrier heights[10–13] of Pd-on-GaAs Schottky contacts. Among them, the Schottky contact of depositing Pd on an atomically clean surface[13] of

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a GaAs substrate showed the lowest value of 0.88 eV. It is reasonable to assume from all the reported barrier heights of 0.88–0.97 eV[10–13] that their interfaces were of phase I/GaAs, i.e., Pd and GaAs have reacted at the interface.

We emphasize the viewpoint that from barrier height measurements and hydrogenation experiments, it is clearly understood whether or not a Pd-on-GaAs interface has reacted.

Quantitative analysis was made on the data of the barrier height change with exposure to hydrogen;[21)]

$$\Delta V = n_d \mu / \varepsilon_0 \quad (4)$$

where ΔV is the variation of the barrier height (in unit V) due to hydrogenation, n_d the density of the dipole, and μ the electrical dipole momentum, respectively. The dipole momentum is assumed as 2×10^{-29} C cm, which is the value of the dipole momentum of a hydrogen s-type adatom (on Ni).[21)] In ref. 21, n_d is written as θN, where θ is the coverage ratio of hydrogen and N the density of the adsorption site. The degree of reaction of Pd and GaAs, which can be controlled by the presence of a native oxide layer, determines the adsorption sites, and hence, the sensitivity to hydrogen (Fig. 8). We obtain the hydrogen density of 10^{14}–10^{15} cm^{-2}. Since interface defects exist, the change causing the variation ΔV should be higher than 10^{14} cm^{-2}, which is within the range of acceptable values.

§5. Conclusions

High (~1.05 eV) and low (~0.88 eV) barrier heights for the Pd-on-GaAs (n-type) Schottky structure are clarified in terms of the metallurgical structure. Namely, (1) A reacted interface in the Pd-on-GaAs system was found to characterize a barrier height of 0.88–0.92 eV (*C-V*) insensitive to hydrogen. This structure is Pd/Pd–Ga–As/GaAs. The intermediate layer of Pd–Ga–As was realized either by heating the chemically etched sample with a native oxide layer or by depositing Pd on the oxide-free GaAs surface. The intermediate layer may happen to emerge in a chemically etched sample without heating, if adequate precautions were not taken during deposition of Pd on GaAs. (2) A native oxide layer on the chemically etched surface of GaAs was found to prevent or retard the reaction of Pd and GaAs. For n-type GaAs, the interface of Pd/oxide/GaAs resulted in a typical barrier height of 1.05 eV (*C-V*). We found that the Schottky barrier was sensitive to hydrogen when the barrier height was higher than a critical value of about 0.96–0.99 eV. In other words, if there exists Pd–Ga–As at the interface, the Schottky barrier is insensitive to hydrogen. The effect is explained in the light of the creation of electrical dipoles at the Pd/oxide interface. The tentative estimated density of hydrogen at the interface is on the order of $>10^{14}$ cm^{-2}.

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References

1) J. Bardeen: Phys. Rev. **71** (1947) 717.
2) J. Tersoff: Phys. Rev. Lett. **52** (1984) 465.
3) J. L. Freeouf and J. M. Woodall: Appl. Phys. Lett. **39** (1981) 727.
4) J. M. Andrews and J. C. Phillips: Phys. Rev. Lett. **35** (1975) 56.
5) L. J. Brillson: Phys. Rev. Lett. **40** (1978) 260.
6) W. E. Spicer, I. L. Lindau, P. R. Skeath, C. Y. Su and P. W. Chye: Phys. Rev. Lett. **44** (1980) 420.
7) W. Schottky: Z. Phys. **118** (1942) 539.
8) B. E. Nieuwenhuys, R. Bouwman and W. M. H. Sachtler: Thin Solid Films **21** (1974) 51.
9) S. Adachi: J. Appl. Phys. **58** (1985) R1.
10) E. Hokelek and G. Y. Robinson: Solid-State Electron. **24** (1980) 99.
11) D. E. Aspnes and A. Heller: J. Vac. Sci. & Technol. **B1** (1983) 602.
12) A. B. McLean and R. H. Williams: J. Phys. C: **21** (1988) 783.
13) N. Newman, M. van Schilfgaarde, T. Kendelwicz, M. D. Williams and W. E. Spicer: Phys. Rev. **B33** (1986) 1146.
14) T. Sands, V. G. Keramidas, R. Gronsky and J. Washburn: Thin Solid Films **136** (1986) 105.
15) T. Sands, V. G. Keramidas, K. M. Yu, J. Washburn and K. Krishnan: J. Appl. Phys. **62** (1987) 2070.
16) T. S. Kuan, J. L. Freeouf, P. E. Batson and E. L. Wilkie: J. Appl. Phys. **58** (1985) 1519.
17) P. Oelhafen, J. L. Freeouf, T. S. Kuan, T. N. Jackson and P. E. Batson: J. Vac. Sci. & Technol. **B1** (1983) 588.
18) A. Kobayashi, T. Sakurai, T. Hashizume and T. Sakata: J. Appl. Phys. **59** (1986) 3448.
19) T. Sands, V. G. Keramidas, A. J. Yu, K. M. Yu, R. Gronsky and J. Washburn: J. Mater. Res. **2** (1987) 262.
20) E. Wicke and H. Brodowsky: *Hydrogen in Metals II, Application-Oriented Properties*, eds. G. Alefeld and J. Volkl, Topics in Applied Physics, Vol. 29 (Springer-Verlag, Berlin, Heidelberg, New York, 1978) p. 73.
21) K. I. Lundstrom, M. S. Shivaraman and C. M. Svensson: J. Appl. Phys. **46** (1975) 3876.
22) I. Lundstrom and T. DiStefano: Surf. Sci. **59** (1976) 23.
23) L.-G. Petersson, H. M. Dannetun, J. Fogelberg and I. Lundstrom: J. Appl. Phys. **58** (1985) 404.
24) S. P. Kowalczyk, J. R. Waldrop and R. W. Grant: Appl. Phys. Lett. **38** (1981) 167.
25) J. Fan, H. Oigawa and Y. Nannichi: Jpn. J. Appl. Phys. **27** (1988) L2125.
26) Y. Nannichi, J. Fan, H. Oigawa and A. Koma: Jpn. J. Appl. Phys. **27** (1988) L2367.
27) S. M. Sze: *Physics of Semiconductor Devices* (John Wiley & Sons, New York, 1981) 2nd ed.
28) M. T. Schmidt, Q. Y. Ma, D. V. Podlesnik, R. M. Osgood and E. S. Yang: J. Vac. Sci. & Technol. **B7** (1989) 980.
29) M. T. Schmidt, D. V. Podlesnik, H. L. Evans, C. F. Yu, E. S. Yang and R. M. Osgood, Jr.: J. Vac. Sci. & Technol. **A6** (1988) 1446.
30) E. H. Rhoderick and R. H. Williams: *Metal-Semiconductor Contacts* (Oxford University Press, Oxford, 1988) 2nd ed.
31) R. B. Childs, J. M. Ruths, T. E. Sullivan and S. J. Fonash: J. Vac. Sci. & Technol. **15** (1978) 1397.
32) M. A. Sobolewski and C. R. Helms: Appl. Phys. Lett. **54** (1989) 638.