ABSTRACT

The characteristics of GaAs Schottky diodes have been discussed in relation to hydrogen-related issues. The surface subjected to atomic hydrogen would be covered with Ga droplets, and the Schottky contacts fabricated on such a surface becomes inhomogeneous. In plasma processing with hydrogen and/or hydride gases, the induced near-surface defects provide positive charges (donor-type defects) regardless of the substrate conductivity type, and significantly modify the effective Schottky barrier height. The estimated built-in-voltage would become larger than the real one due to hydrogen passivation of dopants, and hence the relationship of $SBH_{C-V} > SBH_{I-V}$ is observed.

INTRODUCTION

A Schottky gate contact is a key element of GaAs-related electron devices, such as MESFET and HEMT. The width of the depletion layer expanding into an underlying semiconductor channel is related to the threshold voltage for such devices. The gate leakage current under a reverse bias condition is expected as low as possible. Therefore, it is usually considered that the Schottky barrier height (SBH) is expected as high as possible. Over the past decade, there has been significant progress in understanding mechanisms of Schottky barrier formation, and various new techniques to control the SBH on an atomic scale have been proposed.[1] However, practical Schottky contacts for device application are not devoid of imperfections introduced during device fabrication processes.

On the other hand, hydrogen, one of the most common background impurities, is easily introduced into semiconductors in virtually every step during the processing of semiconductor devices.[2] During dry etching and plasma-assisted deposition of dielectric films, the hydrogen plasma is inevitably excited along with etchant or source gas plasma. The introduction of hydrogen into GaAs is well known to passivate both shallow donor and acceptor impurities. In wet process, it was also discovered that hydrogen easily diffuses into GaAs even at room temperature.[3]

In this paper, I will discuss the characteristics of GaAs Schottky diodes in relation to hydrogen-related issues: (1) surface stoichiometry change, (2) introduction of near-surface defects and (3) deactivation of dopants and bulk defects (see Fig. 1).

INTERFACE INHOMOGENEITY

First, I will discuss the effect of the surface stoichiometry change upon chemical reaction between hydrogen and native oxides on the Schottky contact properties. Atomic hydrogen can be used to remove oxides and carbon-related contaminants from the GaAs surface. However, an H-treatment at relatively low temperatures, e.g., below 300°C, would result in formation of a Ga-rich surface. In fact, Ide an Yamada showed by using temperature-programed desorption (TPD) and low-energy electron diffraction (LEED) measurements that a long-term H-treatment of the oxidized GaAs surface at 210°C results in the formation of metallic Ga.[4] A similar situation can be expected on the GaAs surface in an acidic etching solution, where hydrogen-gas evolution takes place accompanying with GaAs dissolution. The Schottky diode formed on such a non-stoichiometric GaAs surface should be inhomogeneous in its interface.

![Fig. 1](image-url)
We performed the electrochemical experiments as follows: Cathodic pulses (amplitude: $-1.0 \text{ V vs Ag/AgCl}$) were applied to n-GaAs in an $\text{H}_2\text{SO}_4$ solution with pH=2.0 to evolve hydrogen gas on the GaAs surface. Then, electrodeposition of Cu was performed to form Schottky contacts on this surface by adding a solution of CuSO$_4$ to the original $\text{H}_2\text{SO}_4$ solution. The surface morphology and the chemical composition of the surface was examined by using scanning Auger microscopy.

Figure 2(a) shows a typical secondary electron image (SEM) of the GaAs surface after applying cathodic pulse-train (500ms × 1800 shots). We carried out photoanodic etching in the same solution just prior to applying cathodic pulses, and confirm very smooth (less than several nm) and uniform surface by using in situ electrochemical scanning tunneling microscopy (EC-STM). Therefore, the observed inhomogeneity can be attributed to the cathodic reaction of GaAs with hydrogen. Figure 2 (b) shows an Auger electron spectrum in the dark-spot region observed in the SEM image. The As-LMM signal was scarcely seen in the spectrum for the dark spot, while both Ga and As signals were detected in the smooth region. These results indicates that a reductive decomposition of the n-GaAs surface takes place according to the reaction:[5]

\[
\text{GaAs} + 3e^- \rightarrow \text{Ga} + \text{As}^{3-}. \quad (1)
\]

Tiny protrusions in the SEM photograph can also be considered to be Ga droplet. When the pulse width was shortened (500ms → 5ms) or the cathodic voltage was reduced, the number of dark spots dramatically decreased.

Scanning internal-photoemission microscope (IPEM) was applied to the diode fabricated on the GaAs surface covered with Ga droplet. The IPEM technique developed by our group is capable of revealing spatial distribution of Schottky barrier height (SBH). [6][7] Figure 2(c) shows a typical SBH image, where brighter and darker pixels correspond to the regions with higher and lower SBH, respectively. This image shows that the Schottky contacts fabricated on such a Ga-rich surface is inhomogeneous with lower-SBH islands. Such an inhomogeneous Schottky contact is usually referred to as a parallel or mixed contact.[8][9] In the parallel Schottky contact, even a small size patch does significantly affect on the current-voltage ($I$-$V$) characteristics since the thermionic current is in proportion to exponential of the SBH. On the other hand, the built-in-potential determined by the capacitance-voltage ($C$-$V$) measurement is not very sensitive to the existence of the lo-barrier regions. Therefore, the parallel contact might give arise the discrepancy between the SBH values determined by the $I$-$V$ and $C$-$V$ methods. In fact, the relationship of $\text{SBH}_{I-V} (0.97-1.19 \text{ eV}) > \text{SBH}_{C-V} (0.94-0.98 \text{ eV})$ was obtained for the electrochemically formed Cu/n-GaAs diodes.

Near-surface defects

Second, I discuss the effect of defects in the near-surface region. In a plasma processing with hydrogen and/or hydride gases, hydrogen atoms of high concentration ($10^{19}-10^{20} \text{ cm}^{-3}$) are incorporated in the projected range (-10nm), where various kinds of defects (point defects, dislocation loops, platelets, and gas bubbles etc.) might be formed.[2] The experimental results suggest that such near-surface defects provide positive charges...
We tested various GaAs crystals grown by different techniques, including liquid-phase epitaxy (LPE), molecular beam epitaxy (MBE), vapor-phase epitaxy (VPE), boat grown method (BG), horizontal Bridgman (HB), and liquid-encapsulated Czochralski (LEC).[12] These crystals were supposed to provide different off-stoichiometry compositions. The samples were exposed to a hydrogen plasma in a remote RF (13.56 MHz, 50 W) plasma system. The chamber was evacuated below 10^{-6} Torr prior to feeding a hydrogen gas at a pressure of 0.3 Torr. The distance between the glow-discharge plasma and the substrate was 15 cm and the substrate temperature was kept at room temperature.

Figure 3 shows typical $I$-$V$ characteristics of the Schottky barrier diodes fabricated on (a) n-type and (b) p-type substrates before and after a hydrogen plasma exposure at room temperature. During the plasma exposure, the substrates were kept at room temperature and negatively biased (∼100 V) with respect to the ground level. The effective Schottky barrier height (SBH) was lowered for the n-type substrates (0.74→0.57 eV) and vice versa for the p-type substrates (0.61→0.88 eV).

Consider that defects with the same-type charge as the dopant are introduced in the very vicinity of the substrate surface: in this case donor-type surface defects in an n-type substrate. Due to the high concentration of positive charges in the depletion layer, the electric field will increase near the metal-semiconductor interface.[13] Therefore, the image-force lowering contributes the barrier-height reduction. The lowering is approximately given by,

$$\Delta \phi_{\text{Bn}} \approx \frac{q}{\varepsilon_S} \sqrt{\frac{N_{\text{defect}} d}{4\pi}},$$  \hspace{1cm} (2)$$

where $N_{\text{defect}}$ and $d$ are defect concentration and introduced depth, respectively. As the defect concentration further increases, the tunneling effect might become significant. Therefore, the fact that the tunneling current superimposes on the thermionic-emission current means that the SBH value simply derived by the thermionic emission theory becomes lower than the real one and just apparent.

On the other hand, surface defects with the opposite-type charge to the dopant will increase the effective barrier height. This situation is similar to the counter doping to the substrate, for example the base-diffusion into the prefabricated collector region of a Si bipolar transistor. In this case, donor-type surface defects are introduced in a p-type substrate. If the defect concentration exceeds the original acceptor density, the near-surface region is converted to an n-type, and hence an n/p junction will be formed. This junction is not a standard pn-junction with a depletion layer sandwiched by two neutral regions, but a “partial junction” without an n-type neutral region. The n-type depletion region is directly brought into contact with a metal. As the positive space-charge due to the surface defect, $N_{\text{defect}} d$, increases, the downward band-bending in the surface region will be weakened and finally the energy band profile become concave. Therefore, the energy barrier for a hole transport increases as the defect density increases. If $N_{\text{defect}} d >> N_A$ and $N_{\text{defect}} d >> N_A W_{\text{dep}}$, the energy barrier for holes is raised approximately by,[14]

$$\Delta \phi_{\text{Bp}} \approx \frac{q N_{\text{defect}} d^2}{2 \varepsilon_S}.$$ \hspace{1cm} (3)$$

This enhancement of the energy barrier reduces the diode current in both forward and reverse directions, and hence the SBH determined by the $I$-$V$ method becomes apparent and high.

We found that the decreased SBH for n-GaAs was recovered by applying forward bias voltage. On the other hand, no significant change was observed in the samples under a reverse
bias condition (dissipation power was kept at the same level as that the forward-bias experiment) as well as just preserved at room temperature. For p-type samples, we did not found any change upon current flowing in both directions.

DEACTIVATION OF DOPANTS AND DEFECTS

Deactivation of dopants as well as preexisting defects in the region sub-μm deep from the surface will affect the Schottky diode characteristics. Due to the deactivation of dopants, the depletion-layer width increases under a certain applied voltage with concomitant decrease of the measured capacitance (see Fig. 4) Consequently, the estimated built-in-voltage would become larger than the real one. In such a case, the relationship of $SBH_{C-V} > SBH_{I-V}$ is observed. In the previous sections, I have pointed out that the SBH determined by the I-V method very often becomes “just apparent” due to either inhomogeneity or surface modification during processing. Usually, $SBH_{C-V}$ would become much more apparent.

Hydrogen is also known as a deactivator of deep-level defects. If the generation-recombination centers in the original crystal are deactivated by hydrogen, the reverse characteristics of the diode might be improved (see Fig. 3). The dopant passivation is less stable than that of the deep-level defects when the processing temperature is increased. Therefore, it will be possible to find the processing condition for fabricating a good Schottky-gate contacts.

CONCLUSIONS

For practical contacts for device application, processing issues are responsible for the electrical performance of the contact rather than the mechanism of the Fermi-level pinning at the interface. In this article, the characteristics of GaAs Schottky diodes have been discussed in relation to hydrogen-related issues. The surface subjected to hydrogen during device processing would be modified in various manners, and the experimentally observed deviations from the ideal characteristic should be interpreted by taking multiple effects relating to imperfections at or near the interface into account.

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