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The Strong Correlation between Interface Microstructure and Barrier Height in Pt/n-InP Schottky Contacts Formed by an In Situ Electrochemical Process

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Abstract

In order to investigate the correlation between the microstructure of a metal/semiconductor (M/S) interface and the Schottky barrier height (SBH), Pt Schottky contacts were formed on n-type InP by an in situ electrochemical process under various electrochemical conditions; they were then investigated using scanning electron microscopy (SEM), current-voltage (I-V) and capacitance-voltage (C-V) measurements. Electrodeposition resulted in the formation of arrays of nanometer-sized Pt particles whose distribution strongly depended on electrochemical conditions. The SBH values exhibited a strong correlation with the particle distribution, leading to a high SBH value of 0.86 eV under the condition of the most uniform distribution of the smallest particles. The result is discussed from the viewpoint of the disorder-induced gap state (DIGS) model.

KEYWORDS: Schottky barrier, electrochemical process, pulse plating, surface morphology, Pt, InP, SEM, I-V, C-V, DIGS model

1. Introduction

InP and related materials are promising materials for high-speed electronic devices in the millimeter- and micrometer-wave region and optoelectronic devices. However, metal/n-InP contacts generally produce low Schottky barrier heights (SBHs) with large leakage currents. A typical SBH value is around 450 meV [1,2], which is much smaller than the value expected from the difference between the electron affinity of the semiconductor and the metal work function. Furthermore, SBH values can not be increased by using contact metals with large work functions due to the Fermi level pinning phenomenon. Technologically, however, well-controlled stable metal/semiconductor (M/S) interfaces with SBHs are essential for the realization of advanced InP-based electronic devices with high reliability.

We have recently shown that the SBH value of Pt/n-InP contacts can be increased up to 860 meV [3] using an in situ pulsed electrochemical process. This process is also shown to be useful for the Schottky-gate formation in metal semiconductor field-effect transistors (MESFETs) and high electron mobility transistors (HEMTs) [4,5].

The purpose of this study is to optimize the electrochemical process for high SBHs by investigating the correlation between the microstructures of Pt/n-InP interfaces and SBHs. The electrical and structural properties of metal/semiconductor interfaces were characterized by current-voltage (I-V), capacitance-voltage (C-V) and scanning electron microscopy (SEM) techniques. Electrodeposition resulted in the formation of arrays of nanometer-sized Pt particles whose distribution strongly depended on electrochemical conditions. The SBH values exhibited a strong correlation with the particle distribution, leading to a high SBH value of 0.86 eV under the condition of the most uniform distribution of the smallest particles. The result is discussed from the viewpoint of the disorder-induced gap state (DIGS) model.

2. Experimental

The in situ electrochemical process consisted of controlled anodic etching of the semiconductor followed by metal deposition in the same electrolyte including metal ions. For Pt deposition, the following electrolyte was used in this study:

$$1\ \mathrm{M\ HCl\ (200\ ml)+H_2PtCl_6{*}6H_2O(1\ g)+NH_4OH\ [pH=1]}.$$

The electrolyte bath contained three electrodes, i.e., a semiconductor electrode, a Pt counter electrode and a reference saturated calomel electrode (SCE). The potential of the semiconductor electrode is controlled with respect to the SCE reference by a potentiostat with a pulse generator.

A typical current-potential curve obtained at the Pt electrolyte/n-InP interface is shown in Fig. 1. Figure 1 shows that the cathodic currents due to the reduction of Pt ions start to flow around a voltage of -0.5 V with respect to the SCE. The small oscillation in this curve is probably caused by the adsorption of hydrogen molecules generated on the n-InP surface. Other researchers also reported that Pt-film formation could be affected by the H_2-adsorption onto the working electrode [6,7].

The pulse-waveforms shown in Fig. 2 were applied to the n-type semiconductor electrode for the etching of the semiconductor and for metal deposition. In the pulsed mode, the waveforms were adjusted in such a manner that the electrochemical reactions occurred only in the pulse-on time. In this experiment, an avalanche pulse was first applied for the anodic etching, as shown in Fig. 2(a). The anodic pulse etching produces smooth surfaces by repeating the oxidation of the semiconductor surface in pulse-on time and the dissolution of the oxide in the pulse-off time [8].

Immediately after the anodic etching, the plating pulse with an offset d.c. bias Vrd, was applied in order to deposit metal on the semiconductor substrates, as shown in Fig. 2(b). In order to reduce the metal ions only in the pulse-on time, the V_{rd} was set at from -0.4 to -0.5 V, at which cathodic currents do not flow. Use of the pulsed mode instead of the d.c. mode was found to be useful for accurate control of the etched and deposited thickness determined by the number of pulses. Furthermore, it was also found that the pulsed mode improved the current efficiency for metal plating, largely avoiding the problem of H_2-evolution on the semiconductor electrode [3].

In this study, n-type InP bulk wafers with a donor density of $4\mathrm{x}10^{15}$ cm^{-3} were used for the fabrication of Schottky diodes. For the electric current supply, a GeAu/Ni contact layer was first evaporated on the back of an n-InP substrate and then annealed at 370°C in N_2 for 5 min. Photoresist was used as the mask for selective etching and metal deposition. Just prior to starting the electrochemical process, samples were chemically cleaned by H_2SO_4-based etchant in order to remove native oxides from the surface.

The electrical characteristics of the Schottky diodes were investigated by the I-V and C-V techniques. For the I-V techniques, the values of SBH and the ideality factor (n) were obtained using the thermionic emission theory. The value of the effective Richardson constant used for n-InP was 9.6 $\mathrm{Acm^{-2}K^{-2}}$. The morphology of the metal-deposited surface was investigated by SEM (Hitachi S-4100).

3. Results and Discussion

3.1. Electrical characteristics of Schottky diodes

The I-V characteristics of Pt/n-InP Schottky diodes formed by the electrochemical process and those by the conventional electron beam (EB) deposition process are compared in Fig. 3. The EB deposition gave a conventional low SBH value of 0.44 eV with a large n value of 1.7. On the other hand, the electrochemically produced Schottky diodes showed almost ideal thermionic emission characteristics with much higher SBH values and small n values of 1.0-1.1.

The Schottky diode electrochemically produced by the d.c. mode gave an SBH value of 0.63 eV. Pulse-plated diodes gave an even higher SBH value of 0.86 eV. The latter value was near the Mott-Schottky limit for Pt/n-InP contact. Furthermore, as compared with the EB deposition, the pulsed electrochemical process largely reduced the leakage currents of Schottky diodes by more than 7 orders of magnitude at a reverse bias of -2 V.

The I-V characteristics of Pt/n-InP Schottky diodes formed under various electrochemical conditions are compared in further detail in Fig. 4. Table I summarizes the plating conditions including the d.c. bias (V_{rd}), the pulse height (V_{hd}), the pulse period (t_{pd}) and the pulse width (t_{wd}), whose definitions are indicated in Fig. 2. As shown in Fig. 4(a), the electrochemical deposition in the d.c. mode gave different SBH values of 0.52 eV and 0.63 eV at different values of V_{rd}. On the other hand, as shown in Fig. 4(b), SBH values of 0.60 eV, 0.73 eV and 0.86 eV were obtained in the pulsed mode by changing t_{pd} and t_{wd}. These results suggest that SBH values are not pinned but strongly depend on the deposition methods and conditions.

C-V measurements were carried out at 1 MHz. The SBH values obtained from 1/C2-V plots showed good agreement with those obtained by the I-V method in all the diodes electrochemically fabricated in this study. This result indicates that intimate Pt/n-InP contacts without any interfacial layers were formed by the electrochemical process.

3.2. Morphology of Pt/n-InP interfaces

In order to clarify the relationship between SBH and electrochemical conditions, Pt/n-InP contacts were formed under various plating conditions, and the initial surface morphology was investigated in detail by SEM observation. It was observed that nm-sized Pt particles were formed on the InP substrate at the initial stage of the electrochemical deposition. Further deposition did not increase the particle size but increased the number of particles. Eventually, relatively smooth Pt films were formed due to the merging of size-saturated Pt particles in both d.c. and pulsed modes. However, the particle size as well as its distribution were found to strongly depend on applied waveforms. Typical SEM images are shown in Figs. 5(a) and 5(b) for the initial stage of deposition by d.c. and pulsed modes, respectively. The d.c mode resulted in larger sizes and wider size distributions than the pulsed mode. Figure 6 shows the histogram for the distribution of the Pt particle diameter. As shown in Fig. 6, an average particle diameter of 29 nm and rms size deviation of 9 nm were obtained for the d.c. mode. On the other hand, the pulsed mode resulted in a much smaller average particle diameter of 26 nm with a much smaller rms deviation of 3 nm.

The particle diameter and its distribution observed in the initial Pt deposition are plotted in Fig. 7 vs the ratio of pulse widths, t_{wd}, to pulse periods, t_{pd}, of applied pulses. Figure 7 shows that both the average diameter and the width of the diameter distribution became smaller with shorter pulse widths and longer pulse periods. In particular, the diameter distribution was strongly influenced by the ratio of the pulse-on and -off times. This result seems to suggest that, to obtain small and uniform particles, it is important to deposit metal ions quickly, keeping the metal-ion density constant near the electrolyte/semiconductor interface through the recovery of the reduced ions in the pulse-off time. It was also found that the particle size and its distribution width became larger and broader if the offset biases were more negative than -0.5 V. This is because Pt deposition takes place even during the pulse-off time in the d.c. mode, as shown in Fig. 1.

3.3. Correlation between interface microstructure and SBH

The observed SBH values of Pt/n-InP contacts formed by using various electrical conditions are plotted in Fig. 8 vs the observed diameter distributions. As seen in Fig. 8, there exists a strong correlation between the surface morphology and the SBH value, causing a change in the SBH of over 400 meV. The SBH value increases with the size reduction and uniformity improvement of Pt particles on n-InP. The highest SBH value of 0.86 eV obtained by the optimized pulse condition corresponds to smallest and most uniform sizes of Pt particles. As the particle size and its uniformity are improved, the SBH value seems to increase towards the

Mott-Schottky limit for Pt/n-InP.

One of the currently prevailing models for the Schottky barrier formation is the metal-induced gap state (MIGS) model 9). According to the MIGS model, the metal/ semiconductor (M/S) contact suffers from the intrinsic Fermi level pinning due to gap states formed by the penetration of the metal wave function into the semiconductor. Thus, the dependence of the SBH on the surface morphology and the formation process observed in the present study cannot be explained by the MIGS model.

We believe that the present result can be explained by the disorder-induced gap state (DIGS) model 10,11). According to the DIGS model, the formation process of the M/S interface generally induces disorder on the surface of the semiconductor which forms a DIGS continuum near M/S interfaces, resulting in the extrinsic Fermi level pinning. Our previous Raman spectroscopy and X-ray photoemission spectroscopy (XPS) studies indicated that the pulsed electrochemical process produced stress- and oxide-free Pt/n-InP interfaces 3,12). Under optimized conditions for the present low energy electrochemical process, fine metal nano particles seem to be deposited without causing a large degree of disorder on the semiconductor surface. From the viewpoint of the DIGS model, this reduces the density of the DIGS continuum, and realizes an almost pinning-free interface near the Mott-Schottky limit.

4. Conclusions

Pt/n-InP Schottky contacts were formed by the electrochemical process and characterized by the I-V, C-V and SEM techniques. The Schottky diodes formed by the electrochemical process gave higher SBH values than those formed by EB deposition, and showed almost ideal thermionic emission characteristics. The Schottky contacts formed by the electrochemical process had a wide range of SBH values from 520 meV to 860 meV, depending on the electrochemical conditions. Electrodeposition led to the formation of nm-sized particles on the InP surface. As compared with the d.c. mode, the pulsed mode with shorter pulse widths and longer pulse periods generally produced smaller and more uniform particle sizes. The SBH values obtained by the electrochemical process exhibited strong correlations with the metal particle sizes and their uniformities. The smallest average particle diameter of 26 nm with an rms size deviation of 3 nm resulted in the highest SBH value of 860 meV. The observed SBH dependence on the surface structure cannot be explained by the MIGS model. It can be explained by the DIGS model. Thus, the electrochemical process can produce an almost pinning-free nm-scaled M/S interface near the Mott-Schottky limit.

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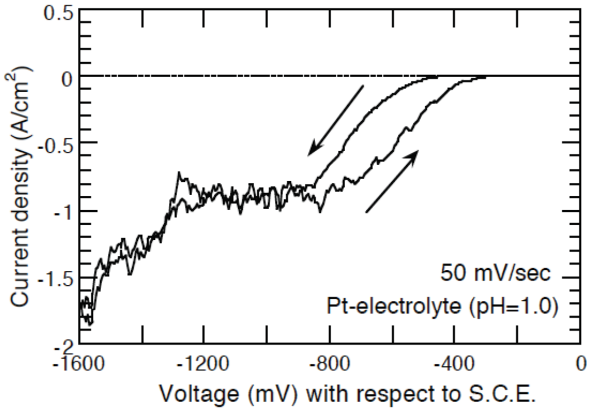


Fig. 1. Current-potential curve with n-InP electrode in Pt electrolyte.

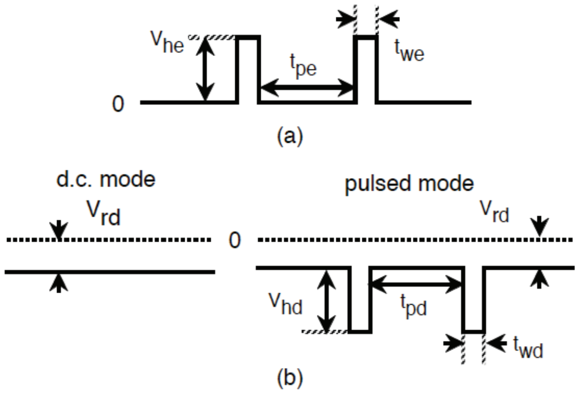


Fig. 2. Applied potential waveforms for (a) anodic etching of semiconductor surfaces and (b) cathodic metal deposition in d.c. and pulsed mode.

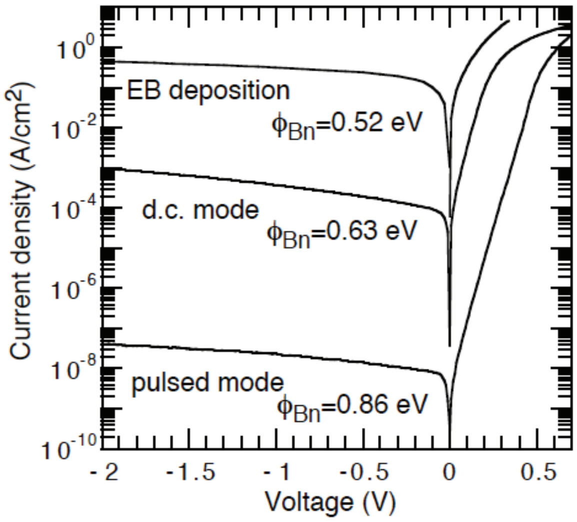


Fig.3. Typical I-V characteristics of Pt/n-InP diodes formed by EB deposition, using d.c. and pulsed modes.

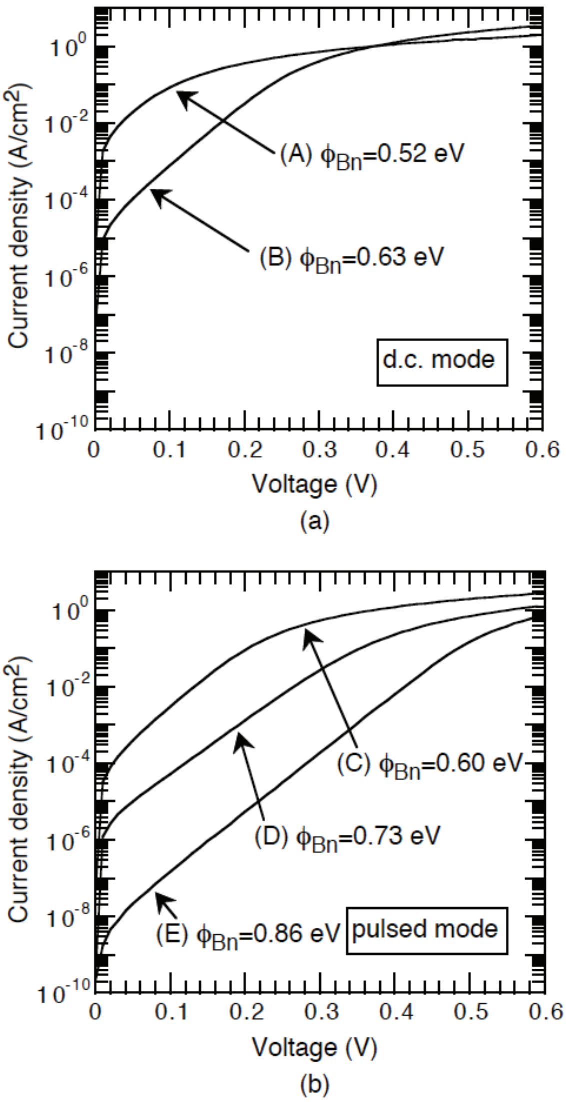
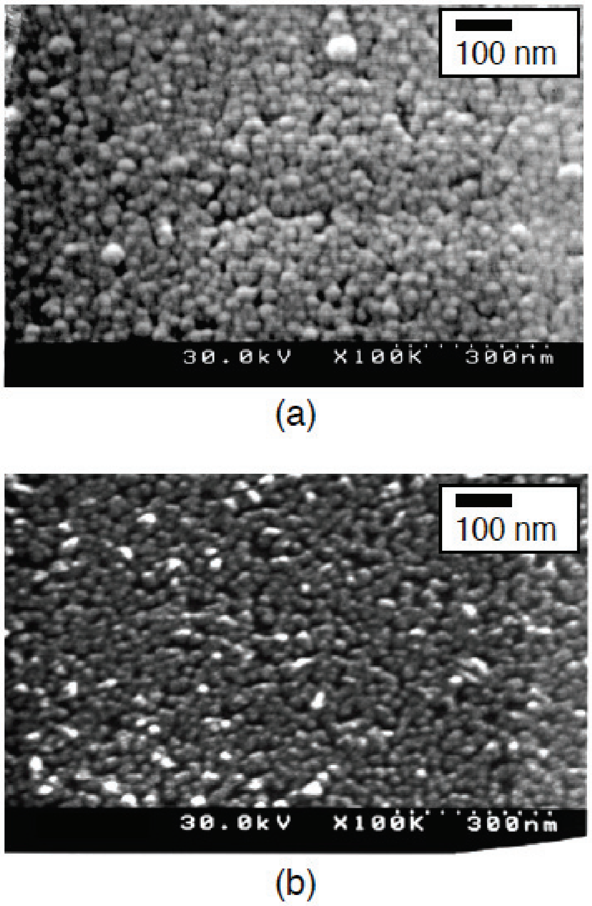


Fig.4. I-V characteristics of Pt/n-InP diodes formed by (a) d.c. and (b) pulsed modes under various electrochemical conditions.

Table 1. Summary of plating conditions for Schottky diode fabrication

Sample no.	Plating conditions			
	V_{rd} (V)	V_{hd} (V)	t_{pd} (μs)	t_{wd} (μs)
A	1.4	—	—	—
B	0.7	—	—	—
C	0.4	1.0	400	100
D	0.4	1.0	200	10
E	0.4	1.0	400	10



(a)

(b)

Fig. 5. SEM images of Pt-deposited n-InP surfaces formed by (a) d.c. mode and (b) pulsed modes.

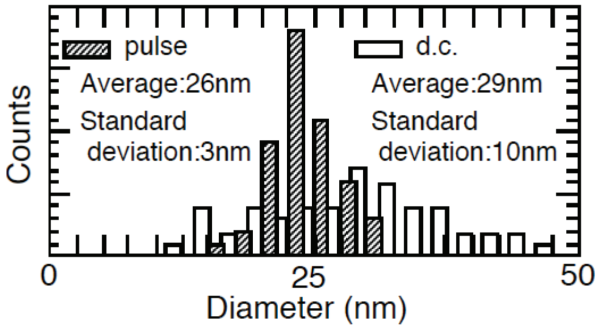


Fig. 6. Typical histogram for distribution of Pt particle diameter produced by d.c. and pulsed modes.

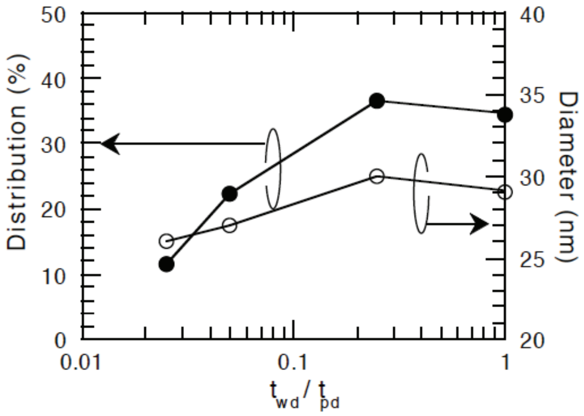


Fig. 7. Plot of average diameter and size distribution of Pt particle vs ratio of pulse width to pulse period in pulsed mode.

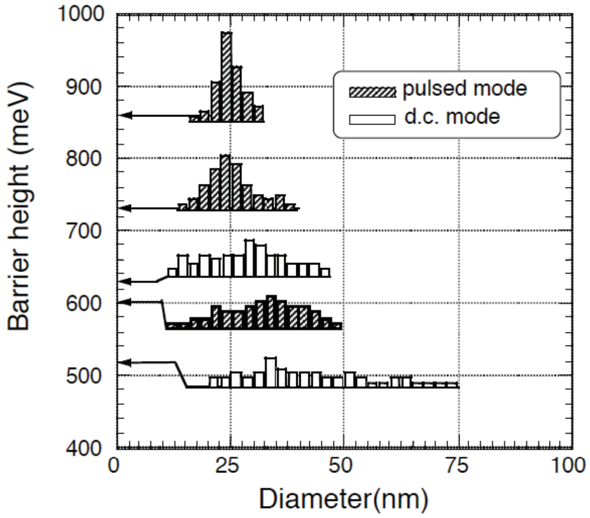


Fig. 8. Correlation between SBH values and the distribution of Pt nanoparticle formed by the electrochemical process.