Title	Current transport and capacitance-voltage characteristics of GaAs and InP nanometer-sized Schottky contacts formed by in situ electrochemical process
Author(s)	Sato, Taketomo; Kasai, Seiya; Hasegawa, Hideki
Citation	Applied Surface Science, 175-176(1-2), 181-186 https://doi.org/10.1016/S0169-4332(01)00059-9
Issue Date	2001
Doc URL	https://hdl.handle.net/2115/14593
Type	journal article
File Information	ASS175-176-2001.pdf

APPLIED SURFACE SCIENCE, 175 (2001) 181

Current Transport and Capacitance-Voltage Characteristics of GaAs and InP Nanometer-Sized Schottky Contacts Formed by *in situ* Electrochemical Process

Taketomo Sato*, Seiya Kasai and Hideki Hasegawa
Graduate School of Electronics and Information Engineering and Research Center for Interface Quantum Electronics, Hokkaido University, Sapporo 060-8628, Japan

*Corresponding author.
Fax: +81-11-716-6004; E-mail address: taketomo@rciqe.hokudai.ac.jp

Abstract

The nanometer-sized Schottky contacts were successively fabricated on n-GaAs and n-InP substrates by the electrochemical process, and their electrical properties were characterized both experimentally and theoretically. From the detailed *I-V* measurements using a conductive AFM system, it was found that the current transport properties of the nanometer-sized Schottky contacts were strongly dependent on metal workfunction, however showed nonlinear *log I-V* characteristics with large n value in range of 1.2 - 2.0 which can not be explained by 1D thermionic emission model. From the theoretical analysis using a computer simulation, it was found that this nonlinear characteristics can be explained by the 3D thermionic emission model with a due consideration of the environmental Fermi level pinning. Furthermore, the calculated *C-V* characteristics showed much smaller movements of the depletion layer with bias underneath the nano-Schottky contacts. These results strongly indicate the importance of controlling the environmental Fermi level pinning to improve the potential controllability of the nano-Schottky contacts.

KEYWORDS: nanometer-sized Schottky contact, GaAs, InP, *I-V* characteristics, *C-V* characteristics, electrochemical process

1. Introduction

Due to scale-down of feature sizes of semiconductor devices and recent increasing interest in quantum devices including quantum wire transistors and single electron transistors, nanometer sized Schottky contacts and ohmic contacts are strongly required. Especially, the nanometer-sized Schottky contacts with tight gate controllability becomes much important to realize reliable device performances, because the number of electrons to be controlled decrease when the device size is reduced into nanometer-sized region. Regarding the formation process of metal/semiconductor (MS) interface, the size- and position-controllability of metal contacts are required as well as the reduction of process induced damage.

With this background, we have recently reported an *in situ* electrochemical process can produce nanometer-sized Schottky contacts in size- and position-controlled fashion and they behaved differently from macroscopic Schottky contacts. Namely, Schottky barrier heights (SBHs) approached to Schottky limit as the size of the contact is reduced in the nanometer range 1). As a result, a high SBH value of 0.86 eV was obtained for Pt/n-InP Schottky contacts which is 0.4 eV larger than the conventional value.

The purpose of this paper is to further clarify the transport properties and the capacitance voltage characteristics of nanometer-sized Schottky contacts both theoretically and experimentally. *I-V* measurements of each of individual nanometer-sized Schottky contacts formed on n-GaAs and n-InP substrates using the in situ electrochemical process [1-5)] were carried out using an atomic force microscopy (AFM) system equipped with a conductive probe. Theoretical analysis of *I-V* and *C-V* characteristics were carried out on the three-dimensional (3D) potential distributions underneath the nanometer-sized Schottky contacts calculated using a successive over relaxation (SOR) method.

2. Fabrication of nano-Schottky contacts

Nanometer-sized Schottky contacts were fabricated using the in situ electrochemical process. The electrochemical process consisted of anodic etching of a semiconductor surface followed by metal deposition in the same acid solution including metal ions. In this study, Sn, Ni, Pt were deposited onto n-type GaAs and n-type InP using the following electrolytes:

Sn: 1M H_2SO_4 (200 ml) + $SnSO_4$ (8 g) [pH=0]
Ni: 1M HCl (200 ml) + $NiSO_4 \cdot 6H_2O$(24g) + $NiCl_2 \cdot 6H_2O$(3 g) [pH=0]
Pt: 1M HCl (200 ml) + $H_2PtCl_6 \cdot 6H_2O$ (1 g) [pH=0].

The electrolyte bath contained three electrodes, i.e., a semiconductor electrode, a Pt counter electrode and a reference saturated calomel electrode (SCE). N-type GaAs wafer with a donor concentration of $2x10^{16}$ cm^{-3} and n-type InP wafer with a donor concentration of $5x10^{16}$ cm^{-3} were used as semiconductor electrodes. For the current supply of the semiconductor electrode, a GeAu/Ni ohmic contact was formed on the back surface of the substrates. In order to remove the native oxide, the semiconductor surfaces were chemically etched just before immersing the samples into the electrolyte.

The potential was applied in pulsed form to the semiconductor electrode for both the anodic etching and the metal deposition. In the pulsed mode, the thickness of surface etching and metal deposition can be controlled by the number of applied pulses. In the initial stage of pulsed electrochemical deposition, nanometer-sized metal particles are formed on the n-type GaAs and n type InP surfaces in a self-assembled fashion [3)]. In this study, the patterned substrates were employed for the selective formation of metal nano-particles as nanometer-sized Schottky contacts. The circular and linear open windows were patterned on the top of the semiconductor surface by standard electron-beam (EB) lithography using JBX-5000LS (JEOL).

Figures 1(a) and 1(b) show the typical SEM images of the Pt nano-dot array and nano wire electrodes fabricated on patterned n-type InP substrates using the in situ electrochemical process. In this study, the electrical properties of metal circular dots were investigated in detail because they seem to be a more basic pattern of the nanometer-sized Schottky contacts. Nanometer-sized metal dots with diameters of 50 nm - 100 nm were formed on the n-GaAs and n InP substrates by controlling the electrochemical conditions.

3. *I-V* measurements using a conductive AFM system

I-V measurements were carried out on each of individual nanometer-sized Schottky contacts using an AFM system equipped with a conductive probe. This system can enable normal AFM observation by the optical lever method and *I-V* measurements between the sample surface and back surface using a HP4156A parameter analyzer (Hewlett Packard, Ltd.) with a current accuracy of 10^{-14} A. The conductive probe is fabricated from highly doped Si covered with thin film of Pt.

Figures 2(a) and 2(b) show the forward log *I-V* curves of the nanometer-sized Schottky contacts formed by the electrochemical process and theoretical log *I-V* curves calculated using thermionic emission model. The diameters of nano-Pt/n-GaAs contact and nano-Pt/n-InP contact were found to be 90 nm and 50 nm, respectively, from SEM observation. For the nanometer-sized Schottky contacts with such small contact area, the electrical analysis at low bias region was difficult because the current values were close to the accuracy level of 10-14 A. The SBH value and n value of nanometer-sized Pt/n-GaAs contacts were estimated to be about 0.80 eV and 1.96, respectively, using the linear log *I-V* region above 0.6 V as seen in Fig. 2(a). Regarding the Pt/n-InP contacts shown in Fig. 2(b), the SBH value and n value were estimated to be 0.67 eV and n value of 1.27. In the both case of Pt/n-GaAs and Pt/n-InP nano-Schottky contacts, the log *I-V* curves showed nonlinear characteristics with large n value which were quite different from the ideal *I-V* curves obtained by 1D thermionic emission model. Moreover, all nanometer-sized Schottky contacts fabricated in present study showed nonlinear log *I-V* characteristics with a large n value in range of 1.2 - 2.0.

One possible reason to explain such nonlinear characteristics is the formation of some interfacial layer at MS interfaces. However, it has been found from the detailed XPS studies [3)] that the in situ electrochemical process can produce intimate MS interfaces without any interfacial layer. Thus, these results suggest that current transport properties of nano-Schottky contacts can not explained by 1D thermionic emission mechanism.

4. Theoretical analysis of electrical properties

In order to clarify the electrical properties of the nanometer-sized Schottky contacts, *I-V* and *C-V* characteristics were theoretically investigated on the basic structure of the nano-Schottky contacts as indicated schematically in Fig. 3. In the traditional analysis of MS interfaces using the one-dimensional (1D) calculation, it is assumed that the potential distribution is laterally uniform in any depth underneath the MS interfaces. However, if the size of an MS contact is made smaller than the depletion width, as shown in Fig. 3, applicability of such a 1D treatment becomes highly questionable. This is particularly so due to the well known fact that the Fermi level is strongly pinned at a certain position in the bandgap on the surrounding free surface. Such a environmental Fermi level pinning is expected to strongly modify the potential distribution underneath the nano metal dots. Using this model, the potential distribution underneath nano-Schottky contacts was calculated by a computer program which solved the 3D Poisson equation using an SOR method. The calculations were carried out using various values of the potential difference at the MS interface, ϕ_{MS}, and diameter, d, of the nano-Schottky contacts. In the calculation for n-type GaAs and n-type InP, the Fermi level position, E_{Fpin}, on the air-exposed free surfaces surrounding the nano-Schottky contacts were assumed to be 0.88 eV and 0.48 eV [6)], respectively, below the bottom of the conduction band edge, E_C.

Figure 4(a) shows the 3D potential distribution of nano-Schottky contact calculated on n InP using $\phi_{MS} = 0.8$ eV and d = 50 nm under the forward bias of 0.6 V. As shown in Fig. 4(a), the potential in the depletion region under the metal dot is greatly modified by the influence of the environmental Fermi-level pinning, resulting in the formation of a saddle point potential at depth of several 10 nm from the MS interface. This is similar to the situation in inhomogeneous Schottky interfaces discussed by Tung [7)]. This potential modification should change the effective barrier height of the nano-Schottky contacts.

Figure 4(b) compares the effective SBH, ϕ_{eff}, of the nano- and macro-Schottky contacts calculated for various forward bias, V. The effective SBH values of macro-Schottky contacts is given by the surface potential of the MS interface, ϕ_{MS} - V. On the other hand, the effective SBH of the nano-Schottky contacts is determined by a saddle point potential when the surface potential of the MS interface, ϕ_{MS} - V, becomes smaller than that of the free surface, E_C - E_{Fpin}. In the case of n-InP nano-Schottky contacts with a diameter of 50 nm, it was found that the effective SBH values became larger than the surface potential, ϕ_{MS} - V above the forward bias around 0.4 V, as shown in Fig. 4(b). The formation of the saddle points reduces the forward current, and should have a large influence on the current transport properties of the nano-Schottky contacts.

The *I-V* curves of the nanometer-sized Schottky contacts were calculated using the potential distribution including the effect of the environmental Fermi level pinning. Basically, the thermionic emission model was used, however, the barrier height to be surmounted by electrons was taken to be a function of the lateral position (x, y) within the metal dot.

The calculated log *I-V* curves of the nanometer-sized Schottky contacts are shown by dotted lines in Figs. 2(a) and 2(b). The theoretical *I-V* curves based on 3D calculation show nonlinear characteristics due to the formation of a saddle point potential, as compared to the ideal curves based on 1D thermionic emission model. The linearity of log *I-V* curves of the nano-Schottky contacts becomes poorer as the contact diameter is reduced. The calculated *I-V* curves based on 3D thermionic emission model show an excellent fitting to the experimental data using the fitting parameter such as ϕ_{MS} of 1.0 eV for n-GaAs contacts and 0.65 eV for n-InP contacts, as shown in Figs 2(a) and 2(b). Thus, it was found that the nonlinear *I-V* characteristics of the nanometer-sized Schottky contacts can be explained by the 3D thermionic emission model including the effect of the environmental Fermi level pinning.

In order to investigate the potential control capability of the nanometer-sized Schottky contacts, the theoretical *C-V* characteristics were calculated using the 3D potential distribution including the effect of the Fermi level pinning. As shown in Fig. 5(a), it was found that the capacitance movement with a reverse bias at the nano-Schottky contact became smaller than that of the macro-Schottky contacts. The *C-V* curves of the nano-Schottky contacts becomes close to the constant capacitance value of the semiconductor free surface with strong Fermi level pinning when the dot size reduced into nanometer range. Figure 5(b) shows the calculated depletion characteristics of n-InP nano-Schottky contacts with a diameter of 50 nm. When the environmental Fermi level is strongly pinned, the depletion width underneath the nano-Schottky contact shows the much smaller movement with a reverse bias. These results indicate that the control of the environmental Fermi-level pinning is necessary to improve the potential controllability of the nanometer-sized Schottky contacts.

5. Workfunction dependence of SBHs in nano-Schottky interfaces

The various nanometer-sized Schottky contacts were fabricated on n-GaAs substrates using the electrochemical process. Figure 6(a) shows the log *I-V* curves of the Pt/, Ni/ and Sn/n-GaAs nano-Schottky contacts with a diameter of 90 nm. The theoretical *I-V* curves showed excellent fitting to all *I-V* curves of the nano-Schottky contacts measured using a conductive AFM system. The contact potentials, ϕ_{MS}, of 1.0 eV, 0.65 eV and 0.52 eV were respectively obtained for the nano-Pt/, Ni/ and Sn/n-GaAs contacts by the theoretical fitting. These obtained SBH values were plotted in Fig. 6(b) vs metal workfunction of the barrier metal. The surface index, S, given by dfBn / dfm was estimated to be 0.38 which was much larger than the theoretical value predicted by metal induced gap state (MIGS) mode 8). These results indicate that the electrochemical process can produce the nanometer-sized Schottky interfaces with reduced Fermi level pinning where the contact potential at MS interface can be controlled by metal workfunction.

6. Conclusions

The nanometer-sized Schottky contacts were successively fabricated on n-GaAs and n-InP substrates by the electrochemical process, and their electrical properties were experimentally and theoretically characterized. The conclusions are listed below.

(1) From the detail *I-V* measurements using a conductive AFM system, it was found that the log *I-V* curves of the nanometer-sized Schottky contacts showed nonlinear characteristics with large n value in range of 1.2 - 2.0. This can not be explained by 1D thermionic emission model.

(2) The calculated theoretical *I-V* curves based on the 3D thermionic emission mechanism with a due consideration of the saddle point showed good agreement with the experimental nonlinear log *I-V* characteristics. Furthermore, the calculated *C-V* characteristics showed much smaller movements of the depletion layer with bias underneath the nano-Schottky contacts. These results strongly indicate the importance of controlling the environmental Fermi level pinning to improve the potential controllability of the nano-Schottky contacts.

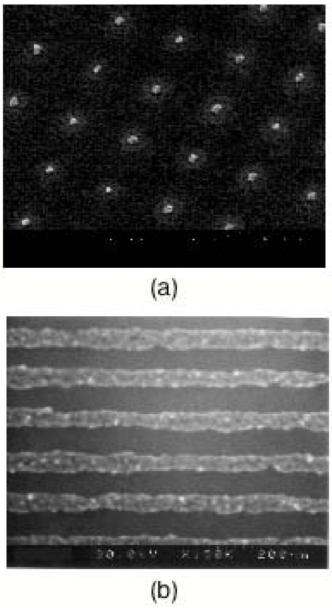
(3) The SBH values of the nano-Schottky contacts fabricated by in situ electrochemical process were strongly dependent on metal workfunction with a slope of 0.38. This result shows the possibility to control SBH by the metal workfunction in wide range for the nano-Schottky interfaces.

Acknowledgement

The present work is supported financially in part by a Grant-in-Aid for Scientific Research B (#09450118) and a Grant-in-Aid for Priority Area Research A (#08247101) both from the Ministry of Education, Science, Sports and Cultures.

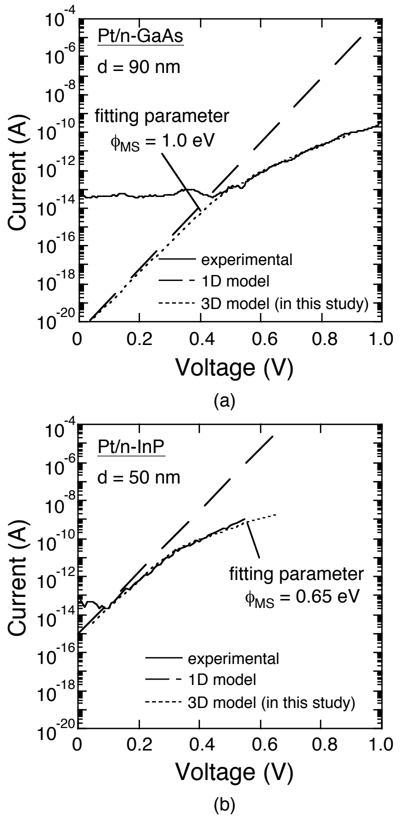
References

1) H. Hasegawa, T. Sato and C. Kaneshiro: J. Vac. Sci. & Technol. B17 (1999) 1856.
2) H. Hasegawa, T. Sato and S. Kasai: ICFSI 1999 accepted for publication in Appl. Surf. Sci.
3) H. Hasegawa, T. Sato and T. Hashizume: J. Vac. Sci. & Technol. B15 (1997) 1227.
4) N. J. Wu, T. Hashizume and H. Hasegawa: Jpn. J. Appl. Phys. 33 (1994) 936.
5) T. Sato, C. Kaneshiro, H. Okada and H. Hasegawa: Jpn. J. Appl. Phys. 38 (1999) 2448.
6) H. Hasegawa and H. Ohno: J. Vac. Sci. & Technol. B4 (1986) 1130.
7) R. T. Tung: Phys. Rev. B45 (1992) 13509.
8) W. Mönch: Appl. Surf. Sci. 92 (1996) 367.


(a)

(b)

Fig. 1 Typical SEM images of nanometer- sized Pt electrodes fabricated on masked n-InP substrates with (a) circular dot pattern and (b) straight line pattern using in situ electrochemical process.



(a)

(b)

Fig. 2 *I-V* curves of nanometer-sized Schottky contacts measured using a conductive AFM system and theoretical *I-V* curves; (a) for n-GaAs and (b) for n-InP.

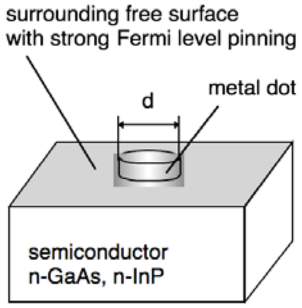
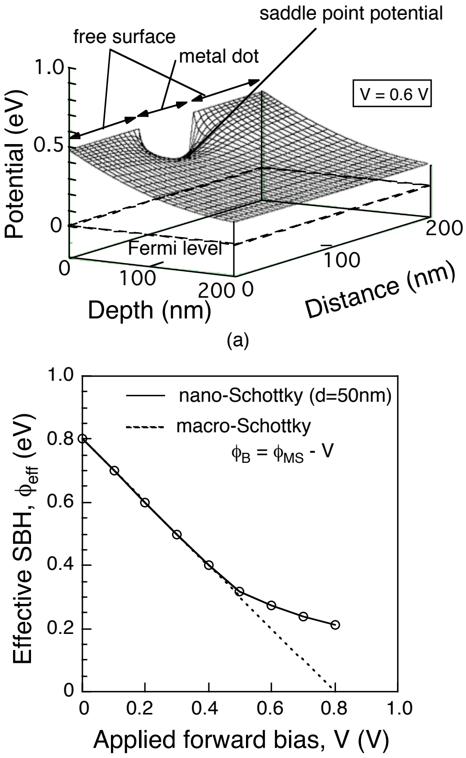


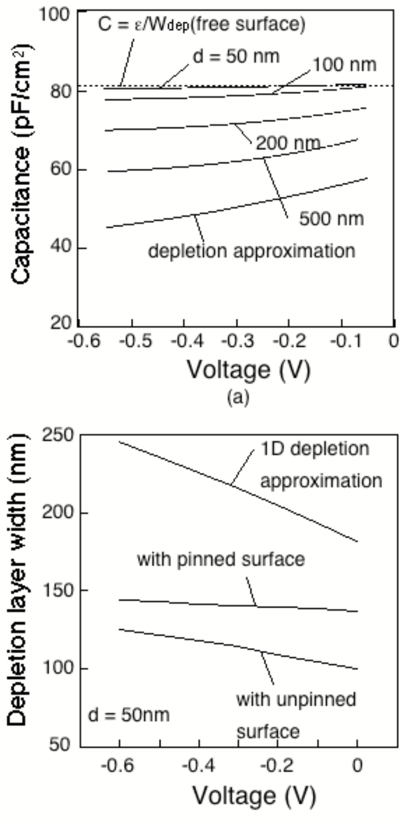
Fig. 3 Sample structure of nanometer-sized Schottky contact for theoretical analysis.



(a)

(b)

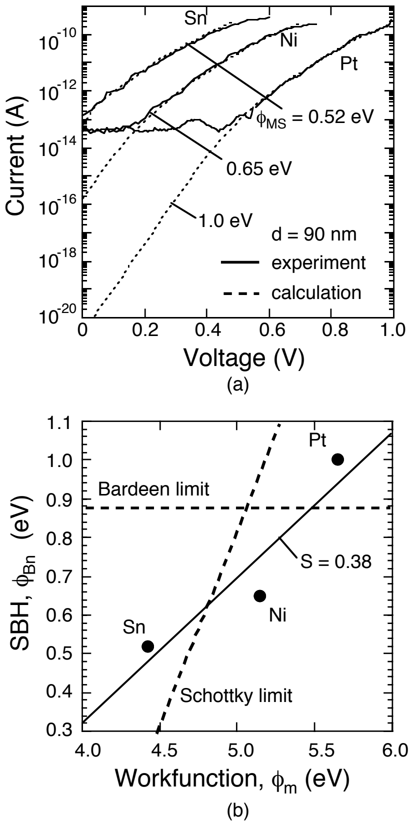
Fig. 4 (a) Potential distribution and (b) effective SBH value of nanometer-sized Schottky contact calculated for n-InP where d = 50 nm, E_C - E_{Fpin} = 0.48 eV and ϕ_{MS} = 0.8 eV.



(a)

(b)

Fig. 5 (a) *C*-*V* characteristics and (b) depletion width of nanometer-sized Schottky contact calculated for n-InP.



(a)

(b)

Fig. 6 (a) *I*-*V* curves and (b) metal work function dependence of SBHs of Pt/, Ni/ and Sn/n GaAs Schottky contacts with 90 nm diameter. A solid line in (b) indicates least square fitting of data.