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Electrical Properties of Nanometer-Sized Schottky Contacts on n-GaAs and n-InP Formed by in situ Electrochemical Process

Taketomo Sato*[1], Seiya Kasai[1], Hiroshi Okada[2] and Hideki Hasegawa[1,2]
[1]*Graduate School of Electronics and Information Engineering and*
[2]*Research Center for Interface Quantum Electronics, Hokkaido University, Sapporo 060-8628, Japan*
*E-mail address: taketomo@rciqe.hokudai.ac.jp

Abstract

The current transport characteristics of nanometer-sized Schottky contacts were investigated from theoretical and experimental viewpoints. A theoretical calculation of the three dimensional (3D) potential distributions showed that the potential shape underneath the nano-Schottky contacts was considerably modified by the surface Fermi level pinning on the air exposed free surfaces, producing a saddle point in the potential. The current-voltage (I-V) curves were strongly influenced by this saddle point potential and resulted in nonlinear log I-V characteristics. Experimentally, the Pt nano-particles were selectively formed using the in situ electrochemical process on n-type GaAs and n-type InP substrates patterned using electron-beam (EB) lithography. Their I-V measurements were carried out using an atomic force microscopy (AFM) system equipped with a conductive probe. The log I-V curves of the nano-Schottky contacts showed nonlinear characteristics with large n values of 1.96 for n-GaAs and 1.27 for n-InP and could be very well explained by the theoretical I-V curves considering the "environmental" Fermi level pinning.

KEYWORDS: nanometer-sized Schottky contact, I-V characteristics, computer simulation, electrochemical process, SEM, AFM, conductive probe, GaAs, InP

1. Introduction

The current-voltage (I-V) characteristics of metal-semiconductor (MS) interfaces show ohmic or Schottky characteristics which have contributed significantly to the construction of all kinds of semiconductor devices such as electronic devices, optoelectronic devices and quantum effect devices. The current transport properties of MS interfaces have been derived from the thermionic emission model to the potential shape at the MS interface which was solved using the one-dimensional (1D) Poisson equation 1). This calculation can excellently reproduce the I-V characteristics of the macroscopic Schottky contacts. In these 1D calculations, the thermionic emission currents were obtained using the assumption that the potential distribution was completely uniform laterally at any position underneath the MS interface.

However, if the size of the MS contact is made smaller than the depletion width underneath, the applicability of such a 1D treatment becomes questionable. This is particularly so due to the well known fact that the Fermi level on all kinds of semiconductor surfaces is strongly pinned at a certain position in the bandgap due to high density surface states whose origin is discussed on the basis of various models 2-6). It is then naturally expected that Fermi level pinning on the free surfaces surrounding such small Schottky contacts will have a large influence on the potential distribution, because the proportion of the contact edge to the contact area becomes larger as the contact area is reduced. Due to the recent increased interest in nanoelectronics, understanding the electrical properties of nanometer-sized Schottky contacts is becoming increasingly important. This is because the scaling down of device dimensions into the nanometer range inevitably requires nanometer-sized metal gates and ohmic contacts.

Being inspired by the importance of these technologies, we have recently studied the electrical properties of such nano-Schottky contacts on compound semiconductors, and have shown that Fermi level pinning at the MS interfaces is greatly reduced. However, a preliminary experimental study has also shown 7,8) that transport properties of nano-Schottky contacts are considerably influenced by Fermi level pinning at surrounding free surfaces.

With this background, the purpose of this paper is to clarify both theoretically and experimentally the detailed transport properties of nanometer-sized Schottky contacts. A theoretical calculation of the three-dimensional (3D) potential distributions underneath the nanometer-sized Schottky contacts with environmental Fermi level pinning was carried out on a computer using a successive over relaxation (SOR) method. Then, theoretical I-V characteristics were calculated using the thermionic emission theory. Experimentally, the nanometer-sized Schottky contacts were fabricated on n-GaAs and n-InP substrates using the in situ electrochemical process 7-11), and I-V measurements of each of individual nano-Schottky contacts were carried out using an atomic force microscopy (AFM) system equipped with a conductive probe. The experimentally observed I-V characteristics were well explained by the theory including environmental Fermi level pinning.

2. Theoretical Analysis of Nanometer-Sized Schottky Interfaces

2.1 Potential distributions

The potential distribution underneath nanometer-sized Schottky contacts was calculated by a computer program which solved the 3D Poisson equation using an SOR method. The calculations were carried out for various values of Schottky barrier heights (SBH), fMS, i.e, the potential difference of the MS interface and for various values of diameter, d, of the nanometer-sized Schottky contacts.

In the calculation for n-type GaAs and n-type InP, the Fermi level position, EFpin, on the air-exposed free surfaces surrounding the nano-Schottky contacts were assumed to be 0.88 eV and 0.48 eV 3), respectively, below the bottom of the conduction band edge, EC. Actually, the surface potential near the metal contact is modified by the charge redistribution, leading to the formation of a transition region between the metal contact and the pinned free surface region. For an accurate calculation of potential distribution, it is necessary to take this effect into account.

However, such a rigorous calculation requires a detailed knowledge of the energy distribution of surface state density and a complicated self-consistent calculation. To our knowledge, no such rigorous calculation has been carried out even for well-known split-gate structures. Traditionally, the boundary condition mentioned in the literature 12-14) for the exposed surface of the split-gate structure was either a constant surface potential or constant surface charge density (frozen charge approximation). Thus, a constant surface potential approximation was employed in this study, as a first approximation.

The maximum charge density on the metal contact is of the order of 1012 ェ q C/cm2 in this study. Since the Fermi level on the free surface is usually pinned near the charge neutrality level by high density surface states of the order of 1013 cm-2, this approximation seems to be a good one, although it slightly overestimates the effect of the environmental Fermi level pinning.

Figures 1(a) and 1(b) show the calculated potential distribution of nanometer-sized Pt/n-GaAs and Pt/n-InP contacts, respectively, for fMS = 0.8 eV and d = 50 nm under the forward bias of 0.6 V. fMS = 0.8 eV may appear too high for n-InP, but it can be realized in nano-Schottky contacts 7). As shown in Figs. 1(a) and 1(b), the potential in the depletion region under the metal dot is greatly modified by the influence of surface Fermi-level pinning. This modification becomes increasingly remarkable as the metal diameter is reduced. Figures 2(a) and 2(b) show the cross-sectional potential profiles of the nanometer-sized Pt/n-GaAs and Pt/n-InP contacts, respectively, for various values of forward bias, V. It is clearly seen in Figs. 2(a) and 2(b) that a saddle point is formed in the potential distribution due to the strong influence of the "environmental" Fermi level pinning in the case of both n-GaAs and n-InP, when the surface potential of the MS interface, fMS - V, becomes smaller than that of the free surface, EC - EFpin. This is similar to the situation in inhomogeneous Schottky interfaces discussed by Tung 15). Furthermore, the saddle point is easily formed on the n-GaAs contacts even at low forward bias, as compared with the n-InP contact. This is because the environmental pinning point, EC - EFpin, at zero bias is higher at the n-GaAs contact than at the n-InP contact. The formation of the saddle points obviously reduces the forward current and, thus should have a large influence on the current transport properties.

2.2 Current transport

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 dot. Then, the effective forward current density at the nanometer-sized Schottky interfaces, Inano, is given by the following equation,

$$I_{nano} = \frac{1}{A}\int_{Dot\cdot area} A^{*}T^{2}\exp\left(-\frac{\phi_{eff}(x,y)}{kT}\right)dxdy \qquad (1)$$

where A* is the Richardson constant, A is the area of the Schottky contact and feff(x,y) is the effective potential barrier to be surmounted under the bias, V, at a lateral position (x, y) in the Schottky contact. The correction for the intrinsic barrier lowering effect due to image force at the MS interface was included.

Figures 3(a) and 3(b) show the calculated I-V characteristics of the nanometer-sized n-GaAs and n-InP Schottky contacts, respectively. The I-V curves of the nanometer-sized Schottky contacts show nonlinear characteristics, as compared to the ideal of the macroscopic Schottky contacts with the ideality factor of unity. The linearity of log I-V curves of the nano-Schottky contacts becomes poorer as the contact diameter is reduced. In the case of n-InP contacts, the slope of log I-V curves of the nanometer-sized Schottky contacts clearly changes around 0.3 V, as seen in Fig. 3(b). This corresponds to the bias V = (fMS - (Ec-EFpin)) / q beyond which a saddle point is formed and the effective barrier height is almost determined by the shape of the saddle point potential. On the other hand, in the case of n-GaAs contacts, the current transport is always controlled by the saddle point potential, because the applied bias always satisfies qV ≥ fMS - (Ec-EFpin) ≈ 0.

Furthermore, the "environmental" Fermi level pinning can reduce the potential barrier thickness at the edge of the nanometer-sized Schottky contacts and this may cause partial current transport by the thermionic field emission mechanism. In the macroscopic Schottky contacts, this can be described by the potential lowering, DfTF, due to the additional tunneling current, according to the thermionic-field emission model by Padovani and Stratton 16). Using this model for the calculation, it was found that this effect becomes appreciable only in the case where fMS is much larger than Ec-EFpin and that the semiconductor is highly doped. Thus, it is negligible for the GaAs and InP samples discussed in this study.

3. Experimental Analysis of Nanometer-Sized Schottky Contacts

3.1 Fabrication of nanometer-sized Schottky contacts

Nanometer-sized Schottky contacts were fabricated using the in situ electrochemical process 7-11). The electrochemical process consisted of anodic etching of a semiconductor surface followed by metal deposition performed by electrochemical reactions at the semiconductor/electrolyte interface. In this study, Pt was deposited onto n-type GaAs and n-type InP using the following electrolytes:

1M HCl (200 ml) + H_2PtCl_6 $6H_2O$ (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 2x1016 cm-3 and n-type InP wafer with a donor concentration of 5x1016 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 9). In this study, the patterned substrates were employed for the selective formation of Pt nano-particles as nanometer-sized Schottky contacts. The dot arrays of circular open windows were patterned on the top of the semiconductor surface with periods of 400 nm by standard electron-beam (EB) lithography using JBX-5000LS (JEOL).

Figure 4 shows the typical SEM images of the Pt dot array fabricated on patterned n-type InP substrates using the in situ electrochemical process. Pt dots were selectively deposited within the open window with a period of 400 nm. It has been reported elsewhere 11) that the size of Pt dots can be controlled by the number of pulses applied during the pulsed electrochemical process. In this study, Pt dots with diameters of 50 nm - 100 nm were formed on the n-GaAs and n-InP substrates by controlling the electrochemical conditions.

3.2 I-V measurements using a conductive probe

In order to investigate the electrical properties, I-V measurements were carried out on each of individual nanometer-sized Schottky contacts using an AFM system equipped with a conductive probe. The setup of a conductive AFM system is schematically shown in Fig. 5. 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. In this study, the I-V measurements were performed both in a line scan mode at constant bias and in a bias sweep mode at fixed probe position. The conductive probe is fabricated from highly doped Si covered with a thin film of Pt. For the electrical analysis, a standard thermionic model was used. The SBH values of the nanometer-sized Schottky contacts were obtained using the Richardson constants of 8.4 Acm-2K-2 for n-GaAs and 9.6 Acm-2K-2 for n-InP.

The typical AFM images of the Pt dot arrays formed on n-GaAs and n-InP are shown in Figs. 6(a) and 6(b), respectively, with the lateral current profiles. The current profiles were obtained on the white lines indicated in the AFM images using the line scan mode while maintaining constant bias. In the case of both n-GaAs and n-InP, electron transport takes place only on the Pt dots. From the current profiles, the diameters of Pt dots formed on n-GaAs and n-InP were estimated to be about 100 nm and 90 nm, respectively, which were almost consistent with those obtained from SEM observation. All current values obtained from the current profile shown in Figs. 6(a) and 6(b) are plotted in Fig. 7 versus applied voltage. For both n-GaAs and n-InP, the I-V curves of the nanometer-sized Schottky contacts clearly showed rectifying behavior due to the formation of a Schottky barrier. In the case of the Pt dot /n-GaAs contacts, reverse currents flowed at forward bias below 0.6 V. The reverse currents at forward bias can be explained by a photovoltaic effect caused by an illumination of laser lights during the AFM measurements.

For the nanometer-sized Pt/n-GaAs and Pt/n-InP contacts, the detailed I-V measurements were performed in a bias sweep mode with fixed probe position at the top of the Pt dot. During the electrical measurements, the laser light was turned off in order to avoid the photovoltaic effect. Figures 8(a) and 8(b) compare the forward log I-V curves of the nanometer-sized Schottky contacts and the macroscopic Schottky contact having a diameter of 400 mm formed under the same electrochemical conditions. 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. As shown in Fig. 8(a), the I-V curves of the macroscopic Pt/n-GaAs Schottky contacts showed ideal thermionic emission characteristics with an SBH value of 1.01 eV and small n value of 1.05. For the nanometer-sized Schottky contacts, 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. 8(a). Regarding the Pt/n-InP contacts shown in Fig. 8(b), the I-V curve of the macroscopic Schottky contact also showed almost ideal thermionic emission characteristics with an SBH value of 0.86 eV and small n value of 1.08. On the other hand, the I-V curves of the nanometer-sized Schottky contact showed nonlinear characteristics, and the SBH value of 0.67 eV and n value of 1.27 were obtained.

4. Discussion

In the case of both the Pt/n-GaAs and Pt/n-InP contacts, the value of the ideality factor, n, of the nanometer-sized Schottky contacts has a tendency to increase as compared with the macroscopic Schottky contacts as determined by the experimental results. These results suggest that the current transport properties at the nanometer-sized Schottky contacts can not be explained by a standard thermionic emission mechanism. However, Figs. 9(a) and 9(b) show the calculated I-V curves based on the ideal thermionic emission model for the nanometer-sized n-GaAs and n-InP Schottky contacts, respectively. The experimental data was also plotted and indicated by the dotted line. As shown in Figs. 9(a) and 9(b), the calculated I-V curve of the Schottky contacts shows an excellent fitting to the experimental data using the SBH value of 1.0 eV for n-GaAs contacts and 0.65 eV for n-InP contacts. Thus, the nonlinear I-V characteristics of the nanometer-sized Schottky contacts can be explained by the thermionic emission model with potential distribution modified by the "environmental" Fermi-level pinning.

The SBH value of 0.65 eV for Pt/n-InP nano-Schottky contact is significantly smaller than that of 0.86 eV in the macro-Schottky contact shown in Fig. 8 (b). This difference can be explained by the difference in dot size for Pt/n-InP Schottky contacts. In our previous study, a strong correlation was observed between the SBH values and the metal dot size. Namely, a strong increase of SBH toward the Mott-Schottky limit was observed with size reduction 7). The macroscopic Pt Schottky contacts on n-InP in Fig. 8(b) consist of metal particles with a diameter of 20 nm. The obtained low SBH value of 0.65 eV is for the nano-Schottky contacts with a much larger dot-diameter of 50 nm, and thus it is consistent with the observed correlation. On the other hand, so far, it has been difficult to realize small particle sizes of 20 nm with a uniform distribution for Pt/GaAs contacts and both of the macro- and nano-Schottky contacts in Fig. 8(a) show similar particle sizes.

The above-mentioned particle size dependence of SBH for InP can be explained by the disorder-induced gap state (DIGS) model 3,7). From the viewpoint of this model, formation of smaller metal particles reduces both the stress at the MS interface and process-induced disorder. This results in the reduction of interface state density and therefore SBH approaches the Mott-Schottky limit. In the case of InP, expected SBH values for the Bardeen limit and Mott-Schottky limit are very different for Pt, the former being 0.48 eV and the latter being 1.1 eV. Thus, a strong particle size dependence of SBH occurs.

These results indicate that the control of the "environmental" Fermi-level pinning becomes increasingly important to obtain good electrical characteristics in Schottky contacts of reduced sizes.

5. Conclusions

The electrical properties of nanometer-sized n-GaAs and n-InP Schottky contacts were investigated from theoretical and experimental viewpoints. The conclusions are listed below.

(1) The computer simulation showed that the potential profile of the nanometer-sized Schottky contacts was considerably modified by the "environmental" Fermi level pinning on the free surface producing a saddle point in the potential distribution. This modification resulted in nonlinear I-V characteristics which were strongly influenced by a saddle point in the potential distribution.

(2) The I-V measurements on the nanometer-sized Pt dot formed on n-GaAs and n-InP by the electrochemical process were carried out using the conductive AFM system. The I-V curves of both the Pt dot /n-GaAs and /n-InP contacts clearly showed a rectifying behavior. However, the log I-V curves of the nanometer-sized Schottky contacts showed highly nonlinear characteristics with a large n value of 1.96 for the n-GaAs contact and 1.27 for the n-InP contact.

(3) The calculated theoretical I-V curves based on the ideal thermionic emission mechanism with a due consideration of the saddle point showed good agreement with the experimental curves and revealed the reason for nonlinear log I-V characteristics of the nanometer-sized Schottky contacts. The present study strongly indicates the importance of controlling the environmental Fermi level pinning to realize well-behaved nanometer-sized Schottky and ohmic contacts.

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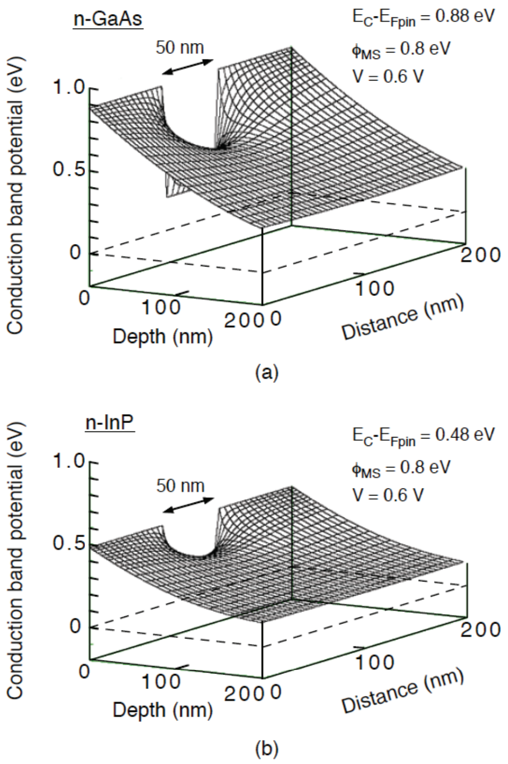


Fig. 1 Potential distribution of nanometer-sized Schottky contacts with 50 nm diameter calculated using a computer program for (a) n-GaAs and (b) n-InP.

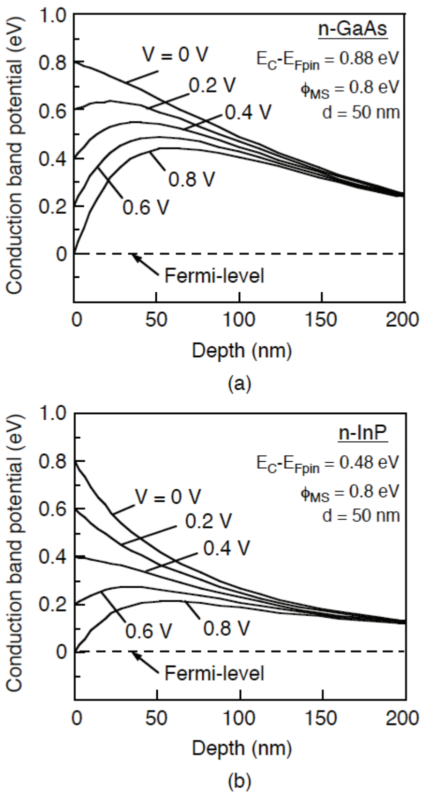


Fig. 2 Cross-sectional potential profiles of the nano-Schottky contact calculated for (a) n-GaAs and (b) n-InP.

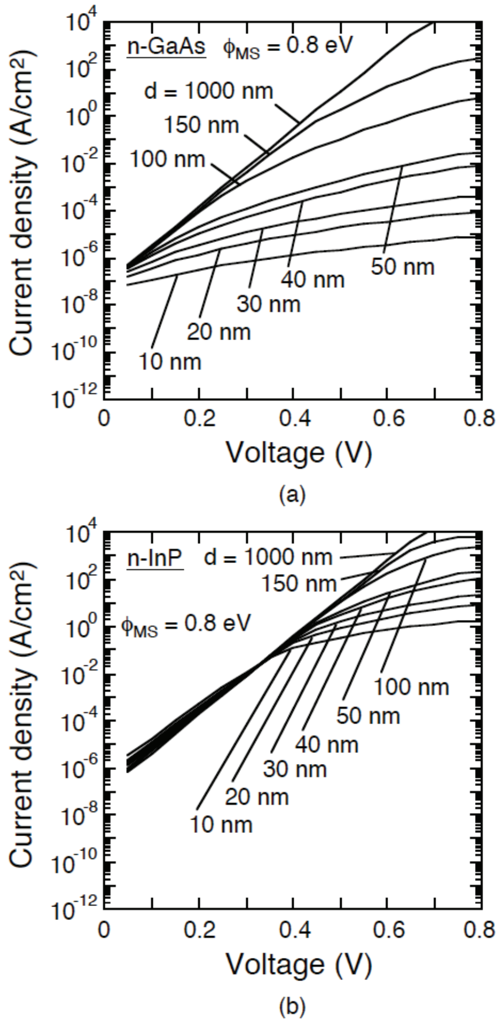


Fig. 3 I-V curves of nanometer-sized Schottky contacts calculated for (a) n-GaAs and (b) n-InP changing the contact diameter.

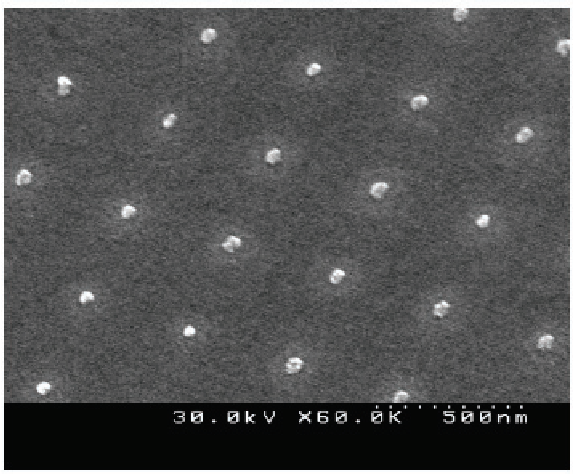


Fig. 4 Typical SEM image of Pt dot array fabricated on the patterned n-InP substrate using the in situ electrochemical process.

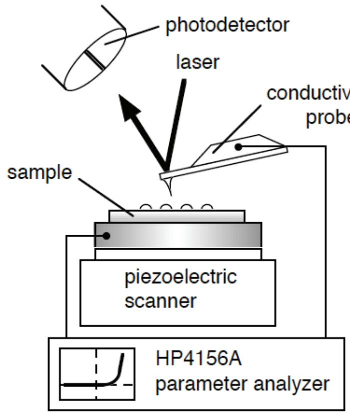


Fig. 5 Setup of an AFM system equipped with a conductive probe. This system provides a normal AFM observation and I-V measurements in the nanometer range.

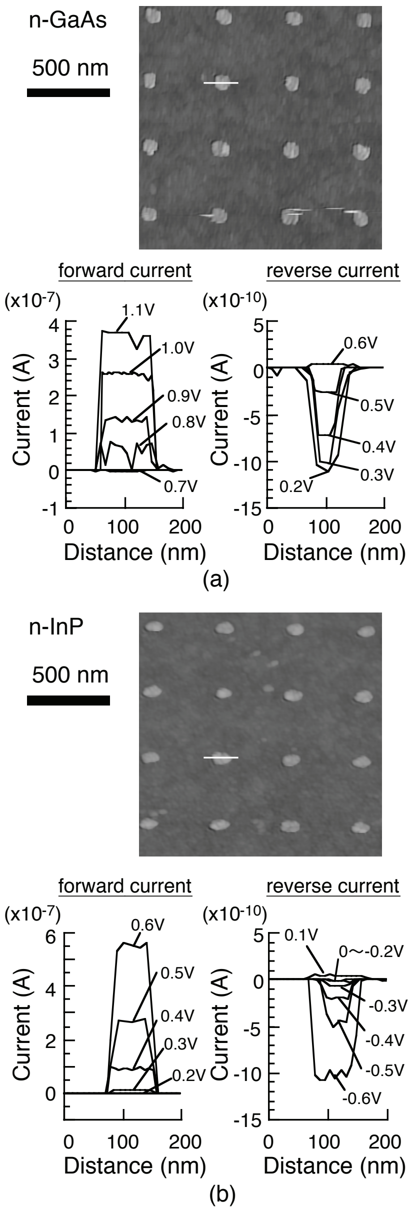


Fig. 6 AFM images of Pt dot array and current profiles obtained from white lines indicated in images; (a) for n-GaAs and (b) for n-InP.

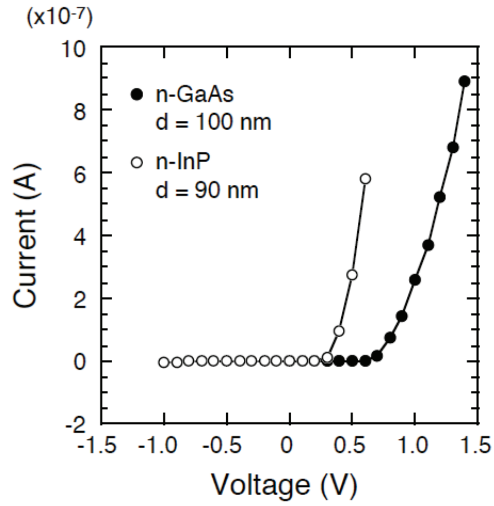


Fig. 7 I-V curves of nanometer-sized Schottky contacts fabricated on n-GaAs and n-InP substrates.

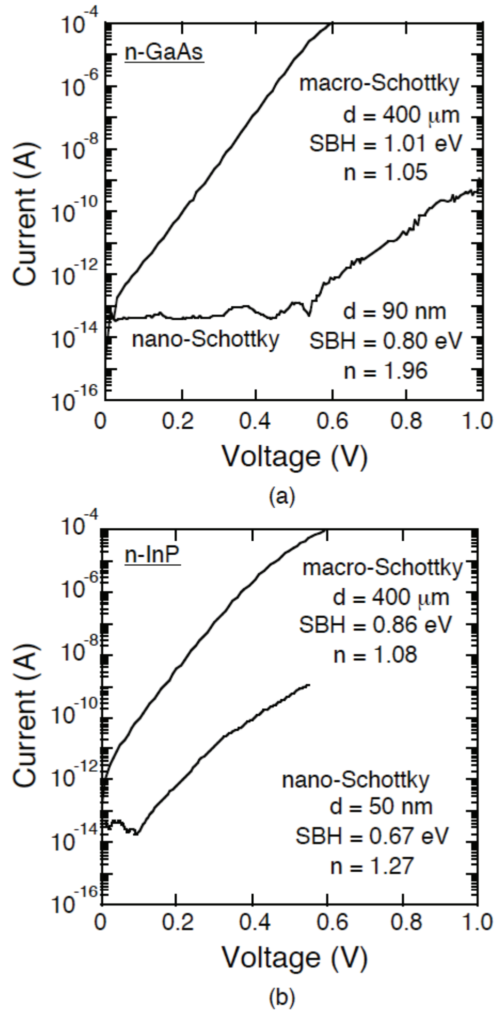
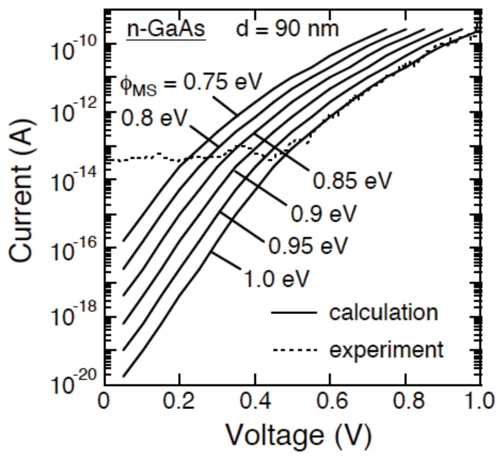
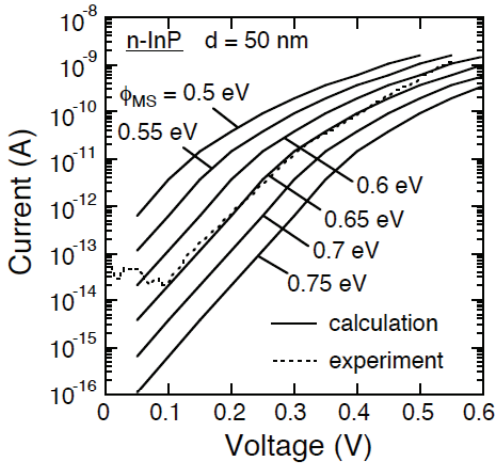


Fig. 8 Typical log I-V characteristics of the macroscopic Schottky contact and the nanometer-sized Schottky contact formed on (a) n-GaAs and (b) n-InP.



(a)



(b)

Fig. 9 logI-V characteristics of nanometer-sized Schottky contacts calculated for (a) n-GaAs and (b) n-InP. Dotted lines show experimental data obtained by conductive probe measurements.