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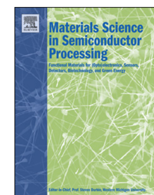
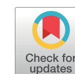


Schottky barrier height modulation effect on n-Ge with TaN contact



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A R T I C L E I N F O

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A B S T R A C T

TaN film with various N contents was formed to provide ohmic contact on n-type Ge. Schottky barrier heights (SBH) of the TaN/n-Ge and TaN/p-Ge contacts were carefully investigated by low-temperature I-V measurement. The SBH was modulated from 0.54 eV for Ta/n-Ge to 0.30 eV for TaN/n-Ge. The SBH lowering on n-Ge was found to be linear with the N contact x in TaN_x, which confirmed the interfacial dipoles layer model. Deposition of TaN on plasma-treated Ge surface showed that the surface damage is not the reason for the low SBH on n-Ge. On the contrary, SBH modulation effect vanished on the rough Ge surface due to deconstruction of the interfacial dipoles layer.

1. Introduction

Germanium is considered as one of the most promising materials in next-generation microelectronic devices because of its high carrier mobility. However, high series resistance caused by the high Schottky barrier height (SBH) of the metal/n-Ge contact restrained the high performance of the devices. The high SBH of metal on n-type Ge arises from the strong Fermi-level pinning effect at the Ge surface [1,2]. In recent study, metallic nitrides such as TiN [3,4] and TaN [5,6] have shown potential ability to realize intrinsic ohmic contact to n-type Ge. The detailed mechanism is ascribed to the interfacial N-Ge dipoles layer formed between Ge and nitride [7] or explained by an amorphous interfacial layer [8]. In this work, TaN/Ge contacts with various nitrogen components were carefully studied to clarify the fundamental physical mechanism. Both the SBH modulation effect and the impact of the Ge surface treatment by plasma on the contact property support the dipoles layer model.

2. Experimental

2.1. Film and structure preparation

Moderately n-type doped and p-type doped Ge(100) substrates both with resistivity of 0.1 Ω cm were firstly cleaned by boiled hydrochloride acid ($HCl:H_2O$ = 1:4 in vol., 103 °C in temperature) for 10 min and then dipped in hydrofluoric acid solution ($HF:H_2O$ = 1:50 in vol.) to remove the native oxide. Ta and TaN thin films were deposited onto these substrates by reactive DC sputtering. Base vacuum pressure of the sputtering system is 1.0×10^{-4} Pa. Tantalum with a purity of 99.99% was used as target. During sputtering, with total gas flow rate of argon and nitrogen fixed at 7.1 sccm, the N_2 flow rate varied from 0.1 to 3.5 sccm to tune composition of the formed TaN film. For comparison, a thin film of pure Ta was also formed by direct sputtering from the Ta target in pure Ar atmosphere. To fabricate contact structure, Ta and TaN were sputtered through a mechanical mask onto the Ge substrates to form contact dots. The formed Ta and TaN dots were 0.8 mm in diameter. Thickness of the TaN dots ranged form 163–235 nm. Thickness of the Ta dots was 240 nm. 300-nm-thick Al were deposited onto the backside of the Ge as ohmic back contact. To avoid mixing or reaction between contact electrodes and Ge, no intentional heating on the Ge substrates was performed during sputtering or before electrical measurement. Thermal stability test was conducted by rechecking the electrical property of the samples after forming gas annealing in mixed Ar/H_2 atmosphere at 300 °C for 30 min.

2.2. Plasma treatment

To perform Ar-N plasma treatment on the Ge surface and study its impact on TaN/n-Ge contact property, n-type Ge wafer were placed on the sputtering target head and received vacuum sputtering. During the 1 min sputtering process, the Ar/N_2 flow rate was set at 3.6 sccm/3.5 sccm, the sputtering DC voltage was 445 V, and the sputtering power density was averaged 4.7 W/cm^2. By a conservative estimation, no less than 100-nm-thick surface Ge was sputtered away form the wafer. These sputtered Ge substrates were immediately sent to deposit Ta/TaN electrode for contact property study.

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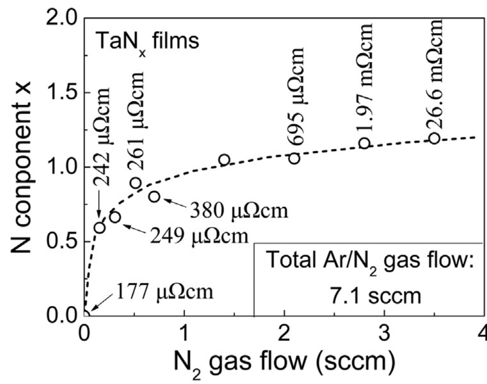


Fig. 1. N component in TaN film (x in TaN_x) with increasing N_2 flow rate. The dashed line is depicted for eye guiding. The labels show the measured film resistivities by four point probes.

2.3. Characterization

Electrical current-voltage (I-V) property was measured both at room temperature and at low temperature with Keithley 2611B sourcemeter and Janis cryostat. Thickness of the TaN film was measured by X-ray relectivity. Film resistivity of the TaN was calculated from the sheet resistance measured by four-point probe and the film thickness. Chemical content of the TaN was checked by Auger electron spectroscopy (AES). Polycrystalline structure of the TaN was scanned by X-ray diffraction (XRD). For the Ge after plasma treatment, surface morphology was observed by atomic force microscopy (AFM).

3. Results and discussion

3.1. Material property of the TaN film

Content of the TaN film is controlled by the Ar/N_2 flow rate ratio during sputtering. Ta atoms can easily react with N ions so that even a little trace of N (0.1 sccm) in the atmosphere resulted in notable N composition in TaN (~$TaN_{0.59}$) as shown in Fig. 1. Along with the increase of the N content until the N_2 flow rate increased to 3.5 sccm, resistivity of the TaN film increases steadily from 242 μΩ cm to final 26.6 mΩ cm. All the TaN film resistivities are higher than that of the pure Ta film (177 μΩ cm).

Fig. 2 shows the X-ray diffraction (XRD, Cu Kα radiation, Rigaku Ultima IV) patterns of the deposited Ta and TaN films (on quartz substrate). The extremely high Ta diffraction (002) and (004) peaks showed a strong texture of tetrahedral β-Ta with its < 002 > direction perpendicular to the growth plane. Trace of cubic Ta can also be detected. According to an early report, the β-Ta are normally formed by sputtering with a resistivity of 180–220 μΩ cm [9]. For TaN, the emerging peaks around 36°, 42°, 60°, and 72° are assignable to the cubic TaN(111), (200), (220), and (311). The cubic lattice remained stable over the whole N content range in TaN_x from x = 0.59 to x = 1.19. Although the cubic lattice property is verified by XRD measurement, the TaN films are actually polycrystalline grains embedded in amorphous TaN matrix due to the low deposition temperature. Detailed information can be found in our previous report on TaN [10].

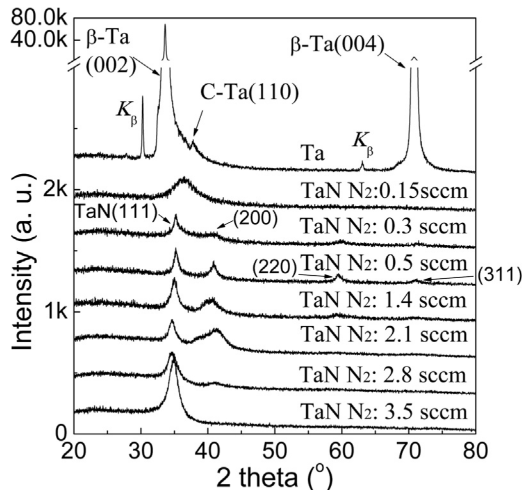
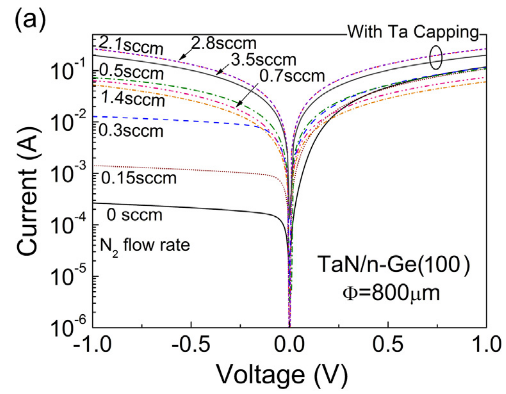


Fig. 2. XRD patterns of Ta and TaN films deposited with different N_2 flow rates. For simplicity of the data, the TaN films were prepared on quartz.



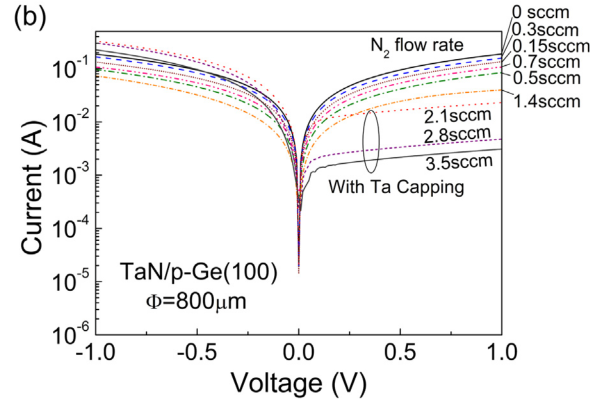


Fig. 3. I-V characteristics of TaN/n-Ge (a) and TaN/p-Ge (b) contacts with TaN films formed with different N_2 flow rates.

3.2. Electrical property of the TaN/Ge contact

Room temperature I-V characteristics of the Ta/Ge and TaN/Ge contacts formed with different N_2 flow rates are shown in Fig. 3. For TaN contact on n-Ge, the rectifying characteristics gradually changed to ohmic property when the N_2 flow rate was increased to 0.5 sccm. Further increase of the N_2 flow rate enlarged the diode series resistance due to high resistivity of the N-rich TaN. To minimize the series resistances in the TaN/n-Ge contacts formed with N_2 flow rates of 2.1, 2.8, and 3.5 sccm, additional 240-nm-thick Ta was sputtered to cap the TaN electrodes. It can be seen that the Ta capped diodes exhibit higher forward currents than the TaN diodes without Ta capping.

For TaN contact on p-Ge, the I-V property remains ohmic until the N_2 flow rate was increased to 1.4 sccm (shown in Fig. 3(b)). With more N incorporation, the high resistivity of the N-rich TaN electrode suppressed the current in both positive and negative-biased directions. By adding Ta capping to the last three TaN/p-Ge contacts, in which the TaN films were deposited with N_2 flow rates of 2.1, 2.8, and 3.5 sccm, all exhibited rectifying characteristics.

In theory, the SBH of a metal-semiconductor contact can be

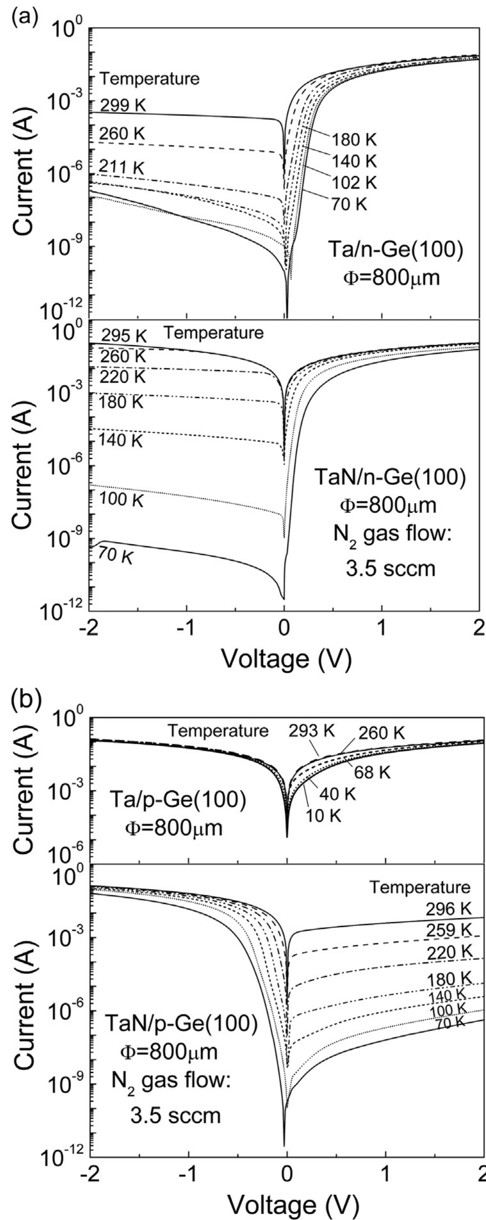


Fig. 4. Low temperature I-V characteristics of Ta contact and Ta-capped TaN contact on n-type Ge (a) and on p-type Ge (b) substrates. The TaN was deposited with N_2 flow rate of 3.5 sccm.

extracted by fitting of the room temperature I-V curves. The well-known thermionic emission model is usually employed for Schottky contact [11]:

$$I = I_S \exp\left(\frac{q(V - IR_S)}{nkT}\right)\left[1 - \exp\left(-\frac{q(V - IR_S)}{kT}\right)\right] \tag{1}$$

in which

$$I_S = AA^* T^2 \exp\left(-\frac{\Phi_B}{kT}\right) \tag{2}$$

where I is the current flowing through the diode, V is the applied bias, q is the absolute charge for electron, T is the temperature in Kelvin, Φ_B is the barrier height for the electrons. A is the contact area, and A^* is Richardson constant which equals 143 A/cm^2 K^2 for n-Ge and 43 A/cm^2 K^2 for p-Ge. The series resistances R_s, the ideality factor n are treated as adjustable parameters. Direct fitting failed for low SBH because linear part of the forward log(I)-V curve was ambiguous. I-V is preferred to be measured at low temperature for larger rectification ratio. The representative low temperature I-V curves for samples of Ta/Ge and TaN/Ge are depicted in Fig. 4.

Table 1
SBHs of TaN contacts on n-type and p-type Ge deposited with various N_2 flow rates.

Sample (N_2 flow rate)	Gaussian mean SBH (eV)	SBH @ 300 K (eV)	SBH by Arrhenius plot (eV)
Contact on n-type Ge(100)			
1 (N_2: 0 sccm)	0.67	0.54	0.39
2 (N_2: 0.3 sccm)	0.48	0.42	0.28
3 (N_2: 0.7 sccm)	0.41	0.37	0.24
4 (N_2: 2.1 sccm)	0.36	0.33	0.19
5 (N_2: 3.5 sccm)	0.33	0.30	0.17
Contact on p-type Ge(100)			
1 (N_2: 0 sccm)	–	–	–
2 (N_2: 0.3 sccm)	–	–	–
3 (N_2: 0.7 sccm)	0.37	0.33	0.18
4 (N_2: 2.1 sccm)	0.44	0.39	–
5 (N_2: 3.5 sccm)	0.54	0.44	0.26

One method to extract the SBH is Arrhenius plot which analyzes *ln* (I/T^2) versus $1/T$. However by Arrhenius plot, we got unreasonably low SBHs as listed in Table 1. From the curve shown in Fig. 3, the reverse biased parts of the current (I_s in formula (2)) were obviously interfered by leakage especially for the several lowest temperatures. Such non-ideality of the I_s currents caused underestimated SBH values when extracted by Arrhenius plot.

On the other hand, forward-biased parts of the I-V curves in Fig. 4 are robust to leakage. Therefore, the measured SBHs can be easily extracted by fitting the forward-biased I-V curves using the above formula (1) and (2). The extracted effective SBH values for five TaN/n-Ge contacts with various TaN compositions are shown in Fig. 5. From Fig. 5, the effective SBH decreased as the diode was cooled down. This lowering effect of SBH with measurement temperature can be explained by assuming lateral inhomogeneity of the Schottky barrier and potential fluctuations at the Schottky interface. The inhomogeneity can be described by assuming a Gaussian distribution of SBH with mean value of $\bar{\Phi}_b$ and standard deviation of σ [12,13]. By this assumption, the effective SBH is predicted to be in a linear relationship with the inverse of temperature which follows the equation:

$$\Phi_{eff} = \bar{\Phi}_B - \frac{\sigma^2}{2kT} \tag{3}$$

In Fig. 5, the SBHs were plotted with the inverse of temperature. By linear fitting of Fig. 5, the Gaussian mean SBHs are extracted and summarized in Table 1. These SBHs are relatively high. For example,

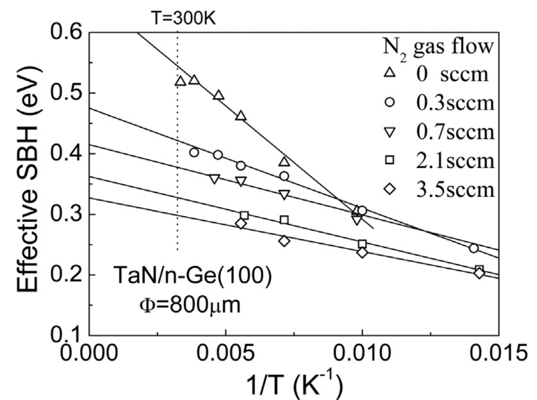


Fig. 5. Extracted SBH values by fitting of the forward parts of the low temperature I-V characteristics for five TaN and Ta contacts on n-type Ge substrate which were deposited with various N_2 flow rates. Linear fittings of the SBHs are shown by black lines.

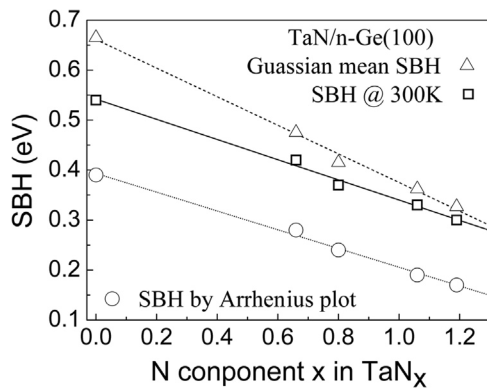


Fig. 6. Gaussian mean SBH, SBH at 300 K, and SBH extracted by Arrhenius for TaN/n-Ge contact are plotted versus the N component x in contact TaN_x films.

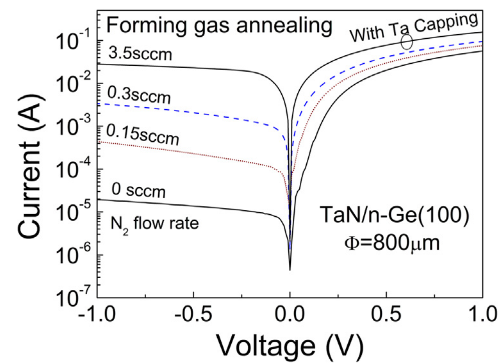


Fig. 7. I-V characteristics of TaN and Ta on n-type Ge substrate after forming gas annealing in mixed Ar/H_2 atmosphere at 300 °C for 30 min. The TaN contact films were deposited with different N_2 flow rates.

the Gaussian mean SBH for Ta/n-Ge is fitted 0.67 eV which is much higher than previously reported 0.51 eV SBH for Ta/n-Ge [1] and nearly equals the Ge band gap. This is probably due to the Gaussian distribution assumption itself which needs careful correction.

For I-V characteristics, the fact that causes a low Schottky barrier to be less rectifying at room temperature is the series resistance. If the series resistance can be reduced to zero, I-V curves may recover their large rectification ratios. And thus, low SBHs can also be extract. Room temperature SBH is of critical importance because most devices work at room temperature. The room temperature SBH can also be evaluated by mathematically extending the low temperature SBH data to ~300 K. In this sense, the Gaussian distribution model finds its value because linear fit of SBH with inverse of temperature was suggested. We reused the fitting lines in Fig. 5 and extrapolate the SBH at 300 K. The data are also shown in Table 1.

By rejudging the SBH at 300 K, the 0.54 eV Ta/n-Ge SBH is then closed to the reported 0.51 eV. Other SBHs for various TaN contacts on n-Ge are ranged from 0.30 eV to 0.42 eV. These room temperature SBHs are found linearly decreased with the increasing N component x in the TaN_x films as shown in Fig. 6. Not only the SBH at 300 K, but also the SBHs extracted by Arrhenius plot and the Gaussian mean SBHs are found to be linearly reducing in Fig. 6. This linearity provides a concrete proof for the interfacial dipoles layer model [7]. The interfacial dipoles layer model assumed a N-Ge dipoles layer at the metallic nitride/Ge interface. The dipoles layer produces an extra electrical potential drop upon the Schottky barrier and then modulates the barrier height. With such a mechanism, the mount of the SBH modulation depends on the dipole density at the interface and the dipole density is proportional to N component x in contact TaN_x film. For metallic nitride contact on Ge, an amorphous interlayer was sometimes observed and the interlayer is used to modulate the contact barrier. But in our case, the amorphous interlayer formation is not clear since our TaN film is partially amorphous too.

To check thermal stability, the TaN/n-Ge contacts in Fig. 3(a) were sent to forming gas annealing. The annealing was conducted in mixed Ar/H_2(5%) atmosphere at 300 °C for 30 min. After annealing, I-V characteristic of each sample was rechecked and found migrating to higher rectification ratio. For instance, the I-V property of the TaN/n-Ge contact with TaN deposited with N_2 flow rate of 3.5 sccm changed from ideally ohmic to a rectification ratio of 10 as shown in Fig. 7. However, the SBH modulation effect by N incorporation can still be remarkably recognized.

Metals usually form ohmic contact on p-type Ge. For Ta/p-Ge contact and TaN/p-Ge contact deposited with N_2 flow rate of 0.3 sccm, their I-V property remained ohmic even when cooled down to extremely low temperatures. The rectification ratios at ± 1 V bias were recorded to be 2 and 8 at 10 K, respectively. As a result, the SBH is too small to be extracted. According to previous investigation, Fermi levels are pinned at a neural charge level which is 0.09 eV above the Ge valence band [1]. As the N content increases in the TaN contact, the low-temperature I-V becomes rectifying and analyzable. The extracted SBH at 300 K is found gradually increased to 0.44 eV for the TaN contact deposited with N_2 flow rate of 3.5 sccm. Fig. 4(b) shows the low-temperature I-V curves of the Ta/p-Ge contact and the TaN/p-Ge contact prepared with N_2 flow rate of 3.5 sccm. The extracted SBH values of the TaN/p-Ge contacts are also listed in Table 1.

3.3. Plasma treatment effect

Finally, we discuss plasma treatment effect on the TaN/Ge contact property. During TaN deposition, the high-energy Ar and N plasma could induce Ge surface defects. The defects could increase the reverse saturation current of the metal/n-Ge contact and possibly turns it to be ohmic-like. To investigate this possibility, we treated our n-type Ge wafers in a harsher mode. They were intentionally placed on the target head and used as target to receive Ar and N ions sputtering. In such a way, much more defects are produced in the Ge substrate if compared to the deposition process in which the wafer is placed 10 cm away from the glowing plasma area. The damage resulted from direct sputtering are much severer than the suspected defects during deposition. The sputtering condition was already described in the experimental part. Ar/N_2 mixture gas was used during sputtering to simulate the TaN deposition process. But the Ge surface nitridation effect is ignored because Ge can only be nitridized at elevated temperature when exposed to N plasma [14]. Even if the Ge wafer may be nitridized, the surface layer was continuously removed by plasma bombardment.

However, the sputtering is not homogeneous. According to the sputtering operation theory, the target received densest bombardment between the magnetic poles, and received sparse bombardment near the poles.

Then the Ge wafer was deposited arrays of TaN or Ta contacts to check their I-V property. Considering the inhomogeneous plasma treatment, I-V properties of the deposited TaN contact arrays were carefully examined form row to row and from dot to dot. Spacing between each two dots in a row is 2 mm. Typical I-V curves measured from a five-dot row of the TaN/n-Ge contact (with Ta capping) are depicted in Fig. 8. Marks of 1–5 correspond to the dot number in the row. AFM morphology was scanned on the Ge surface of the five dots before TaN deposition. As shown in Fig. 9, the Ge surface morphology changed from mirror-flat to wavelike from dot 1 to dot 5. The RMS roughness is estimated to be 0.24 nm, 0.26 nm, 0.35 nm, 1.19 nm, and 19.6 nm for each. Along with the surface morphology changing, the I-V property migrated from ohmic to rectifying. This result is fully out of our expectation. In general opinion, surface roughness and damages usually lead to higher leakage current. But as shown here, the reverse current decreased with stronger plasma treatment!

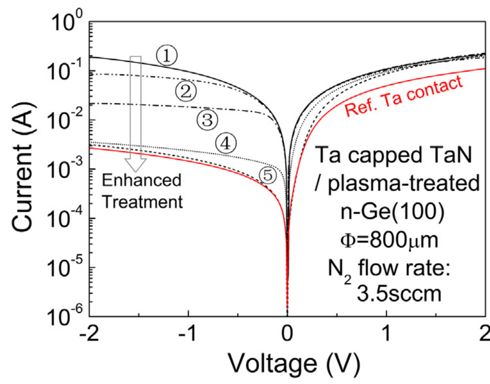


Fig. 8. I-V characteristics of Ta capped TaN contacts on n-Ge substrate. The n-Ge substrate received plasma treatment before contact deposition. The TaN was deposited with N_2 flow rate of 3.5 sccm. Label 1–5 denoted the dot sequence in the row. On the same plasma-treated Ge substrate, Ta/n-Ge(100) contact showed a typical I-V curve as reference.

This unexpected phenomenon can be explained by taking the interfacial dipoles model into consideration. In contact of TaN on pristine Ge(100) substrate, the nitride/Ge interface are assumed to be smooth and flat. The N-Ge dipoles are generally arranged parallel across the interface. The resulted ordered dipoles layer strongly modulate the local energy band shape and the SBH. But for plasma treated Ge, bombardment of ions not only leave visible surface waviness as viewed by the AFM images, but also nanoscale surface roughness, which is depicted in Fig. 9(F). On such a rough Ge surface, the N-Ge dipoles are disordered in their orientations. Without order parallel arrangement, the dipoles lost their ability to modulate the local energy band shape. And without ordered dipoles layer, the nitride/n-Ge contact finally retreated back to the initial high SBH governed by Fermi-level pinning. Therefore, the assumed N-Ge dipoles layer are comprehended to be highly dependent on the morphological flatness of the TaN/Ge interface.

On the other hand, Ta/n-Ge contact did not show any obvious dependence on the sputtered Ge surface roughness. Typical I-V curve of Ta on sputtered n-Ge is depicted in Fig. 8 as reference. It is interesting to find that the I-V curve follows the curve for dot 5 in a very similar way except that the forward current is somewhat lower. Such a coincidence indicates that the N-Ge dipoles layer completely vanished in dot 5. The difference in forward current level can be reasonably explained by the higher resistance of β-phase Ta grown on Ge than the cubic α-phase Ta grown on TaN [10,15]. Both I-V curves are simulated to extract SBH of 0.53 eV with ideality factor n = 1.6. The 0.53 eV SBH is similar to the SBH of Ta/n-Ge contact without plasma treatment (I-V shown in Fig. 3(a), SBH = 0.52 eV with n = 1.1). But the ideality factor n = 1.6 is higher, and the reverse current is increased by one order of magnitude due to the rough Ta/Ge interface. As a summary to above observation and discussions, the interfacial dipoles layer rather than the interface defect which should be responsible for the Fermi-level de-pinning and

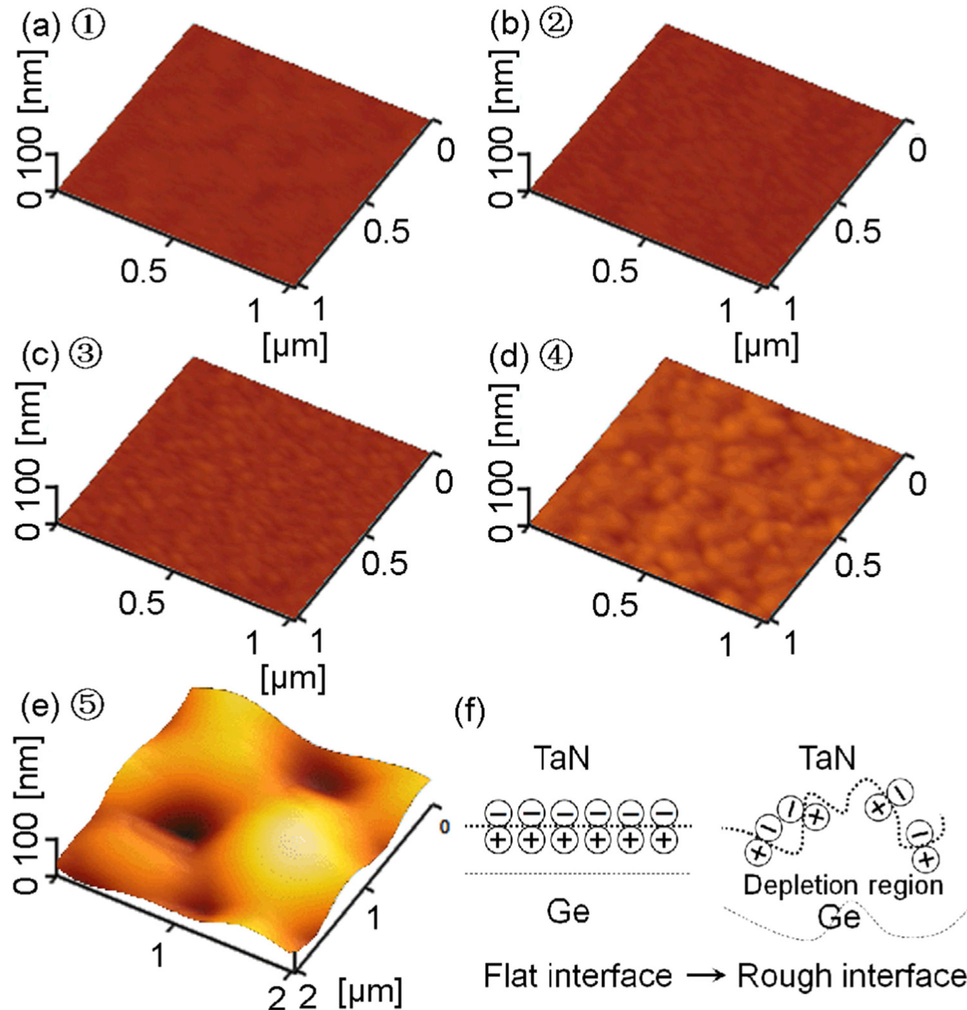


Fig. 9. (a)–(e) AFM morphology scanned on plasma-treated Ge surface before TaN contact deposition. Images numbered 1–5 correspond to the five dots with their I-V curves shown in Fig. 8. (f) schematic figure showing impact of interface roughness on the N-Ge dipoles layer in TaN/n-Ge contact.

the SBH modulation effect in TaN/n-Ge.

4. Conclusion

TaN/Ge contact was investigated on both n-type and p-type Ge. By analyzing the low-temperature I-V characteristics, the SBH of TaN/n-Ge was found modulated from 0.54 eV for Ta/n-Ge to 0.30 eV for TaN/n-Ge. Correspondingly for contact on p-type Ge, the SBH was found to increase to 0.44 eV. These data are also compared to the other two methods to extract SBH, which are Arrhenius plot and Gaussian distribution model. All the SBHs were found to be linearly changing with the N content x in TaN_x. The linearly relationship between SBH lowering versus N content x provides reasonable support for the interfacial dipoles layer model which assumed an interfacial N-Ge dipoles layer at the nitride/Ge contact. Further more, the deposition of TaN on plasma treated Ge surface shows that the roughness of the Ge surface deconstructed the interfacial dipoles layer and diminished the SBH modulation effect.

Acknowledgments

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