Characterization on photoelectric property of TiN/Si heterojunction

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Highly-sensitive photovoltaic effect of TiN/Si heterojunction has been reported. The junction exhibited a high photovoltaic sensitivity (PVS) of 57 mV/mW to He-Ne laser illumination when the laser spot was incident onto the Si substrate. The change of Schottky barrier height due to illumination has been discussed. However, when the laser spot was incident on the TiN film surface, the PVS was only 0.71 mV/mW, which was mainly attributed to the low transmittance of TiN film to He-Ne photons. And further, when a UV Hg lamp irradiated the TiN film, the PVS was enhanced much and increased up to 421 mV/mW.

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1. Introduction

Titanium nitride (TiN), as a face-centered cubic interstitial compound, has attracted much attention due to its superior properties such as high melting point (2950 °C), low electrical resistivity (10^{-5}-10^{-2} Ωcm), high surface hardness (2000 kgf/mm^2), and good chemical inertness [1-4]. TiN thin films are used extensively as protective and decorative coatings, and particularly as diffusion barriers in the microelectronics industry. In Si semiconductor technology, TiN has a good bonding to Si substrate very well and has promising applications in contact metallization [5]. TiN/Si junction has been studied by some groups [6-14]. Much work has been concentrated on the growth or physical properties of TiN thin film. However, the work on the photoelectric property of the heterojunction is rather limited. In this letter, we will report on the photoelectric characteristics of TiN/Si junction in our recent research.

2. Experiments

TiN film with thickness of 100 nm was deposited on a p-type silicon (001) substrate by a computer-controlled laser molecular-epitaxy system. Detailed growth procedures can be found elsewhere [11]. The in situ reflection high-energy electron diffraction and ex situ x-ray diffraction indicated an epitaxial growth of the TiN film on the Si substrate. Atomic force microscope measurement shows that TiN film surface is smooth with root mean square roughness only 0.842 nm over a 10×10 μm^2 area. The resistivity and mobility of TiN film are 3.6×10^{-5} Ωcm and 583.0 cm^2/Vs by Hall measurement [11]. The total area of the junction is 2×4 mm^2. In contacts were sputtered onto the top of the TiN film and the bottom of Si substrate. The area of electrical contacts is 1 mm^2. The current-voltage characteristic of the TiN/Si junction was measured by a pulse-modulated current source. A 632.8 nm He-Ne laser with power density of 1 mW/mm^2 was adopted as light source. The He-Ne laser spot is 7 mm^2 in area. The photovoltaic response was recorded by a 500 MHz digital oscilloscope with an input impedance of 1 MΩ. All the electrical measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 displays the current density versus voltage (J-V) characteristic of the junction. It shows a typical Schottky diode behavior. The schematic measurement circuit is shown in the right inset of Fig. 1. Forward bias is defined as a positive voltage applied on the p-type Si. In Fig. 1, the square and circle symbols denote the current measured in the darkness and under irradiation by a He-Ne laser, respectively. The Schottky junction demonstrates a striking rectification. In the darkness, the ratio of forward and reverse currents reached 1300 in the applied voltage range from -0.9 V to 0.9 V. The dark current was about 27 μA at -1 V. When a He-Ne laser spot was incident on the Si substrate, the J-V curve shifted downward with a large photocurrent occurring at the reverse bias. The photocurrent reached 350 μA at -1 V bias. The open-circuit voltage V_{OC} was 400 mV and the short-circuit current J_{SC} was 35.3 mA/cm^2. From the formula $\eta=(J_{SC}/q)/(L/h\nu)$ [14], where L is incident laser power density, h Planck constant, ν the laser frequency, and q the charge for one electron, the external quantum efficiency η can be calculated to be 10%. The left inset shows an expanded view of the J-V curves in Fig. 1.

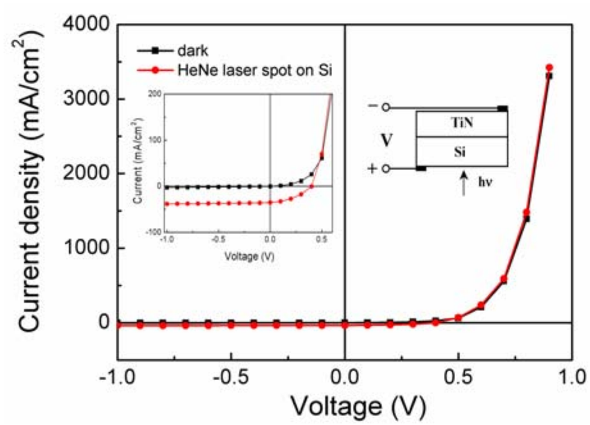

Fig. 1. The current density-voltage relations of TiN/Si heterojunction in the darkness and under illumination of a He-Ne laser. Left inset is an expanded view of the J-V curves, and right inset is a layout of the device for measurement.

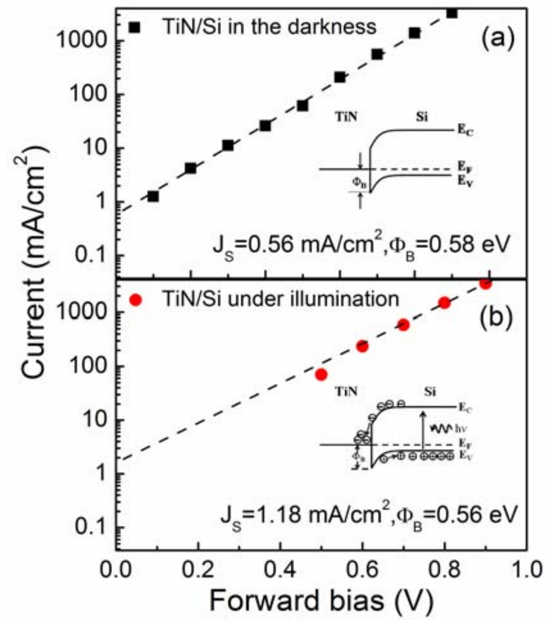

Fig. 2. Forward current vs. applied voltage of TiN/Si heterojunction measured (a) in the darkness and (b) under illumination in semi-log plot. The dashed line is a linear fitting line of experimental data.

The current transport behavior of a Schottky junction is often characterized by a thermionic emission model. The current density J is expressed as $J = J_S\left[\exp(\frac{qV}{nkT}) - 1\right]$ [15], where J_S is the saturation current density, V the applied voltage, n the ideal factor, k the Boltzmann constant, and T the absolute temperature. J_S can be obtained from the intercept by extrapolating the linear portion of ln$J$ to V=0 as shown in Fig. 2 (a) and (b) [16]. The Schottky barrier height Φ_B of our heterojunction at zero bias can be determined from J_S by the formula $\Phi_B = \frac{kT}{q}\ln(\frac{A^{**}T^2}{J_S})$, where A^{**} is an effective Richardson constant. Assuming A^{**}=32 A/cm^{2}K^2 [9], Φ_B can be deduced to be 0.58 eV in the darkness which is in agreement with the results in other reports [9,17]. The Schottky barrier of 0.56 eV under illumination can be obtained in the same way, and it decreased by 0.02 eV. The change of Schottky barrier should be related with the injection of photo-generated carriers. As shown in the inset of Fig. 2(b), under illumination, the holes concentration in Si increases and the Fermi level lowers down and are more close to conduction band of E_v, so the Schottky barrier decreases.

Fig. 3a and b show photovoltaic signals recorded directly by the 500 MHz oscilloscope. The diode exhibited a large open-circuit photovoltage of 400 mV when the He-Ne laser spot was illuminated on the Si wafer (as shown in Fig. 3a. The photovoltage was consistent with the open-circuit voltage V_{OC} deduced from the current-voltage curve under illumination. The photovoltage mechanism of the Schottky junction can be understood by the following process. TiN is a highly conductive material with carriers concentration of 7.437×10^{19} /cm^3. When it was connected with Si (hole concentration of 1.45×10^{15} /cm^3), a space charge electric-field was built up at the interface and distributed at Si side. The width of space charge region could be estimated by the formula $W = \sqrt{2\varepsilon_s V_{bi}/qN_D}$ [16], where ε_s is the dielectric constant of Si, V_{bi} the built-in electric voltage, q the charge for one electron and N_D the carriers concentration of Si. The width of space charge region is about 0.52 μm. Under He-Ne laser illumination, electrons in the valence band of Si absorbed the photons and made transition into the conduction band. Thus holes in the valence band and electrons in the conduction band were created, respectively. Those excess carriers created in the space charge region or within one diffusion length near space charge region can be separated by the built-in field. Then electrons were swept into the TiN film and holes were left in the Si substrate. Eventually, a photovoltage between the two electrodes appeared. The photovoltaic sensitivity (PVS), defined as photovoltage/on-sample power, was 57 mV/mW. However, when the laser spot was illuminated on the TiN film, the open-circuit photovoltage was only 5 mV (as shown in Fig. 3b and the corresponding PVS was 0.71 mV/mW.

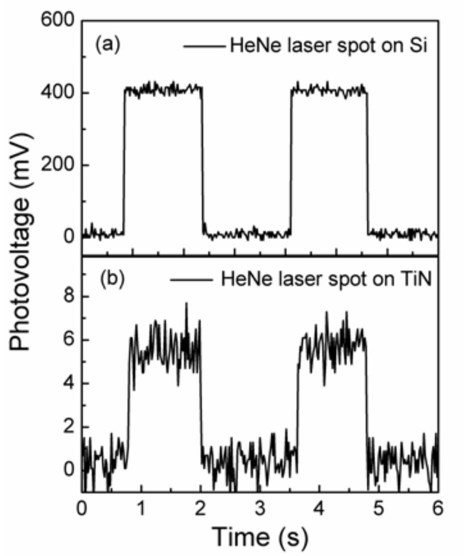

Fig. 3. The open-circuit photovoltage of the TiN/Si junction when a He-Ne laser spot was incident on (a) the Si substrate and (b) the TiN film surface, respectively.

The PVS of the junction under He-Ne laser illumination from film surface was much lower than that from Si substrate. To explain the results, we measured the transmittance spectrum of TiN film. We deposited TiN film with thickness of 100 nm on MgO substrate under the same experimental conditions. The transmittance of the TiN film at 632.8 nm was only 20% as shown in Fig. 4. It means that only a little part of the incident photons could penetrate TiN film to enter the space charge region at Si side under film-side illumination. However, when the laser spot was incident onto the Si substrate, Si absorbed almost all incident He-Ne photons to generate electrons and holes. Based on the formula $L = (k_0 \mu T \tau / q)^{1/2}$ [16], where L is the diffusion length, k_0 the Boltzmann constant, μ the mobility, T the absolute temperature, τ the lifetime of electrons, we can get a diffusion length of about 0.7 mm by inserting the mobility μ of 1450 cm^2/Vs and the carrier lifetime τ of ~ 130 μs [16]. The diffusion length of 0.7 mm is larger than the thickness of Si substrate (~0.4 mm), which indicates that the majority of photo-generated electrons could diffuse into the space charge region before recombination with holes. Then, in space charge region, the electrons were driven to the TiN film by the electric field and were effectively separated from holes. So, the photoelectric signal under Si-side illumination was higher than the signal measured under film-side illumination.

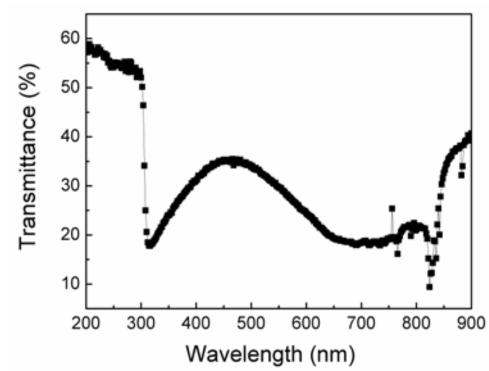

Fig. 4. The transmittance of TiN film with a thickness of 100 nm.

From Fig. 4, we also find that the transmittance of the TiN film in the range of 200-300 nm is higher. If a UV light with wavelength between 200-300 nm is incident on the TiN film of the junction, the photovoltage should be improved. Therefore we adopted a monochromatic Hg lamp with wavelength of 253.65 nm to illuminate the junction. The light power density was 0.0187 mW/mm^2 with a light spot area of 8 mm^2. An open-circuit photovoltage of 63 mV was achieved as shown in Fig. 5. The PVS was 421 mV/mW, which is six hundred times of 0.71 mV/mW obtained under He-Ne laser illumination. So, it is reasonable to conclude that the transmittance of TiN film really plays an important role in the photoelectric process of the Schottky junction when the junction is under illumination from film side. High transmittance of the film determines that more photons can arrive at the space charge region, where photo-generated carriers can be absorbed fully and separated effectively.

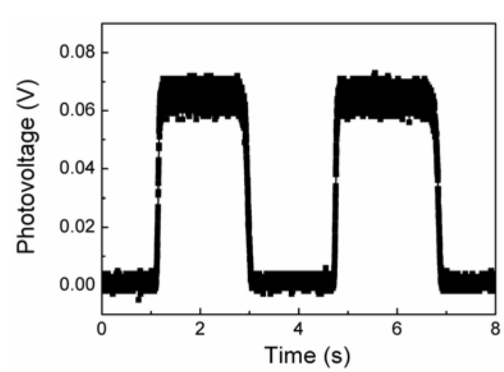

Fig. 5. The open-circuit photovoltage of the TiN/Si junction when the TiN film was illuminated by a Hg lamp.

4. Conclusions

In summary, the photoelectric property of TiN/Si junction has been investigated in detail. When a He-Ne laser with power density of 1 mW/mm^2 irradiated the Si substrate of the junction, an open-circuit voltage of 400 mV and a short-circuit current density of 35.3 mA/cm^2 has been obtained. The external quantum efficiency was 10%. The Schottky barrier height of junction derived from current-voltage curve under He-Ne laser illumination was 0.56 eV compared with 0.58 eV in the darkness. The change of barrier height was related to the photo-generated carriers' injection. When a UV light with wavelength of 253.65 nm was illuminated on the TiN film surface, the open-circuit photovoltage was 63 mV and the corresponding sensitivity was 421 mV/mW. Our experimental results show that the TiN/Si junction has a high photovoltaic response to both visible light and the UV light. Therefore, it has promising applications in photodetection.

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