Non-equipotential effect observed on the surface of Ti/Si under uniform illumination

Chunlian Mei1,2,3, Shuai Liu4,5, Anhua Dong1,2, Xu Huang1,2, Chongqi Yu1 and Hui Wang1,2,5

1 State Key Laboratory of Advanced Optical Communication Systems and Networks, School of Physics and Astronomy, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People’s Republic of China
2 Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People’s Republic of China
3 Chongqing No. 8 Secondary School, No. 96, Xiaolongkan Main Street, Shapingba, Chongqing 400030, People’s Republic of China
4 School of Science, North University of China, No. 3, Xueyuan Road, Taiyuan, ShanXi 030051, People’s Republic of China
5 Authors to whom any correspondence should be addressed.
E-mail: billliu198826@hotmail.com and huowang@sjtu.edu.cn

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Abstract

In this letter, a non-equipotential surface photovoltaic effect is reported in nano metal–semiconductor structures. When the surface of the Ti/Si is uniformly illuminated by a beam of light, a controllable surface photovoltaic effect is observed on the metal side. The center of the surface presents a remarkably higher metallic potential than the surrounding region. The surface photovoltage is detected to be as high as 53 mV. Besides, it depends sensitively on the thickness and size of the metal films, demonstrating it is a unique feature of nano metal films. We ascribe this phenomenon to the boundary effect of photon-generated carriers in the ultrathin metal thickness. The theoretical calculations based on equivalent electron diffusion model are in great agreement with the experimental results. The results may promise some novel applications based on the nanoscale metal–semiconductor systems.

1. Introduction

Electronic behavior in low-dimensional nanostructures, like metal particles, islands and films, is substantially different from that of bulk materials [1–5]. As the nanofabrication technique advances, materials with surface effects and quantum-size effects have attracted attention of researchers [6–9]. Consequently, a lot of novel and exotic physical and chemical characteristics of ultrathin films and nanotextures have been widely reported recently [10–13]. The related studies are of great importance for the application of nanotechnology in electronic devices as well as fundamental understanding of nanoscience [3].

Here, we report a remarkable light-induced non-equipotential effect observed on the surface of nano metal films. In general, metals are always equipotential. This phenomenon commonly exists in thick layered and bulk materials. However, in the condition of titanium nano films (Ti/Si), the effect is featured by a central-high metallic potential, which means that the center of the surface presents a remarkably higher potential than the surrounding region when the surface of the metal side is illuminated by a beam of light. The surface potentials have been observed in plasmonic metal nanostructures [14, 15], two-dimensional semiconducting nanocrystals [16] and ferroelectric materials [17]. The previous reports indicate that the surface potential effect is significant and can be widely applied to novel photoelectric devices. The non-equipotential effect in this letter is sensitive to the metal thickness and so different from the physical properties of conventional metal systems, which may promise opportunities for some novel applications,
such as boundary optimization of photoelectric sensors, designing electronic printing template based on potential difference and evaluating nanoscale ultra-thin metal films.

2. Results and discussion

The Ti films with various thicknesses were fabricated on n-type monocrystalline Si(111) substrates (0.3 mm in thickness) by DC magnetron sputtering at room temperature. The resistivity of Si is around 50–80 $\Omega$ cm, which is lightly doped by phosphorus with a density approximate to $5.36 \times 10^{13}$ to $8.64 \times 10^{13}$ cm$^{-3}$. The native surface oxide layer of the Si was removed by a dip in dilute HF (1%). Then the Si substrates were cut into rectangles before sputtering. The base pressure of the vacuum system was $5.0 \times 10^{-5}$ Pa. During the deposition, the pressure of argon gas and the DC power were maintained at 0.60 Pa and 20 W, respectively. The deposition rate of Ti, measured by a stylus profile meter on thick calibration samples, was about 0.2 Å s$^{-1}$. The Ti thickness was controlled by adjusting the sputtering time.

In the process of measurement, the whole surface of the sample was illuminated uniformly by a cold light source, which consisted of light ranging from 450 nm to 700 nm. The electrodes (about 0.5 mm in diameter) on the films were made by alloying indium with copper wires to avoid measurable rectifying behavior. As shown in figure 1(a), one of the contacts is fixed at the centre of the sample surface, the other can be moved along x-axis or y-axis. All the measurements were performed in a dark room to avoid spurious illumination by a high-performance digital multimeter.

We first investigated a 10 mm $\times$ 5 mm sample with Ti thickness of 6.0 nm (figure 1(b)). When it was illuminated uniformly by a cold light with a power of $p = 128$ mW cm$^{-2}$, the Ti side showed an obvious non-equipotential effect. Figure 2 shows the electric potential on the Ti surface as a function of position. Obviously, the center of the surface presents a remarkably higher potential than the surrounding region.

We define a surface photovoltage as $\Delta = V_{\text{max}} - V_{\text{min}}$ to describe this phenomenon. In this case, $\Delta$ reaches 48 mV in x direction ($y = 2.5$ mm) and 16 mV in y direction ($x = 5.0$ mm). Namely, a lateral electric field is induced along the surface. This is entirely conflicting with the equipotential state in which the electric field is perpendicular to the metal surface. Therefore, $2\Delta/L$ is defined as an average lateral electric field intensity to describe the non-equipotential effect, where $L$ is the length (or width) of the sample. Accordingly, $2\Delta/L$ reaches 9.6 mV mm$^{-1}$ and 6.4 mV mm$^{-1}$ in x and y directions, respectively.
Figure 3. Experimental (circular icons) and theoretical (lines) results. (a) Metallic potentials as a function of x position on the surface of Ti(6.0 nm)/Si (L × 5 mm rectangles) with different metal lengths L. (b) Surface photovoltage Δ and average lateral electric field intensity 2Δ/L in Ti(6.0 nm)/Si (L × 5 mm rectangles) as a function of the length L. (c) Δ in Ti/Si (10 mm × 5 mm rectangles) as a function of metal thickness, where the inset shows the optimal metal thickness corresponding to metal length. The light power in (a)–(c) is fixed at 128 mW cm$^{-2}$ (d) Δ in Ti(6.0 nm)/Si (10 mm × 5 mm rectangle) as a function of light power. The theoretical parameters are chosen as α = 5 × 10$^{-3}$, β = 2.5 × 10$^4$, d$_0$ = 5.5 nm and C = 0.7.

We further measured the surface potential of Ti(6.0 nm)/Si as a function of the sample length L. The width in y direction was fixed at 5 mm and the length L in x direction varied from 6 mm to 20 mm. As the spherical symbols show in figure 3(a), the potential seems to become flat near the middle when the metal length increases, showing a tendency of equipotential effect. The surface photovoltage Δ increases from 40 mV to 53 mV. On the contrary, the average lateral electric field intensity 2Δ/L decreases from 13.4 mV mm$^{-1}$ to 5.4 mV mm$^{-1}$ (figure 3(b)). The results demonstrate that a smaller metal surface suits a more obvious non-equipotential effect. Additionally, we found that Δ is sensitive to metal thickness d. In the case of L = 10 mm and p = 128 mW cm$^{-2}$ (figure 3(c)), Δ decreases sharply as Ti thickness is adjusted away from 6.0 nm. It may suggest an optimum value d$_{opt}$ of Ti for a remarkable non-equipotential effect. In addition, d$_{opt}$ shifts with the length L and they exhibit an approximately linear relationship as the inset of figure 3(c) shows. Figure 3(d) shows the relation between the surface photovoltage and the light power. The non-equipotential effect can be observed even if the light is weak. Obviously, the surface photovoltage increases with the increment of the power but is quickly saturated.

Besides, under the same measuring condition, the surface photovoltages were detected to be 26 mV in Co(4.0 nm)/Si and 12 mV in Cu(3.0 nm)/Si. Thus, there is evidence that the non-equipotential effect is ubiquitous and may exist in different kinds of nano metal films.

Based on the results above, we propose the following boundary effect based on diffusion model to interpret the mechanism behind this surface photovoltaic effect. Generally, when a metal is attached to a semiconductor, a Schottky field will be formed near the interface of metal–semiconductor structure [18]. Electron–hole pairs will be generated locally if a point light irradiates on the metal surface. Those excited electrons will soon transit from semiconductor into metal film by Schottky field with holes remaining in the semiconductor (figure 4(a)). The original density of light-induced electrons is defined as $N_0$, which can be divided into two parts $N_1$ and $N_2$.

$$N_0 = N_1 + N_2 = C_1((h\nu - \phi)^n/h\nu + C_2((h\nu - E_g)^m$$  \hspace{1cm} (1)

$N_1$ is the hot electron flux and can be described as $C_1((h\nu - \phi)^n/h\nu$ according to Fowler’s law [19, 20], where $C_1$ is proportional coefficient, $\nu$ is photon frequency, $\phi$ is Schottky barrier and $n = 2$ for most metals [21–23]. $N_2$ is the electron–hole excitation flux and can be written as $C_2((h\nu - E_g)^m$ according to absorption theory [24], where $C_2$ is another proportional coefficient, $E_g$ is the energy gap of Si and $m$ is an exponential coefficient. The work function of Ti is 4.33 eV and electron affinity of Si is approximately 4.05 eV, so the Schottky barrier should be 0.28 eV. In the process of measurement, the whole surface of the sample was illuminated uniformly by a cold light source, which consisted of light ranging from 450 nm to
700 nm. The photon energy that ranges from 1.77 eV to 2.76 eV is higher than Si energy gap of 1.12 eV. Thus, \( N_2 \) offers a more contribution than \( N_1 \) due to the high photon energy in this effect.

According to the diffusion theory [25, 26], the excited electrons, the original density of which is defined as \( N_0 \), can easily spread laterally away from the original point along the metal surface. The diffusion equation can be written as \( \frac{d^2N(x)}{dx^2} = \frac{N(x)}{\tau_m} \), where \( D_m \) is the diffusion constant in the metal film, \( \tau_m \) is the life time of non-equilibrium electrons in the metal film. Thus the distribution of the carriers at position \( x \) can be calculated as \( N(x) = N_0 \exp(-x/\lambda) \), where \( \lambda = \sqrt{D_m\tau_m} \) is the electron diffusion length in metal film. This is the fundamental mechanism of lateral photovoltaic effect which has been reported a lot [27–31].

The uniform illumination discussed in this work can be identified with the modeling of hundreds of thousands of point lights. Considering a simplified one-dimension situation, the electron density at the position \( x \) is derived from all the lights between the edges. It can be described as \( N(x) = \int_{0}^{L} N_0 e^{-x/\lambda} dr \), where \( r \) is the position of the point light and the bounds of integration reveal the boundaries of the sample. Although \( N(x) \) is caused by every equivalent point light source theoretically, the light-induced carriers which are far from the position \( x \) make no contribution to \( N(x) \) due to the exponential diffusion model. Thus, the valid limits of the integral are the areas very close to the position \( x \). Consequently, in the central region of the sample surface, the carrier density seems to be the same due to the superposition of the same valid ranges and the symmetrical surrounding light sources, as shown in figure 4(b). When it gets closer to the edges or corners of the rectangular sample, the valid illuminated region will be smaller. As shown in figure 4(c), there is a missing part compared with the central area. Therefore, the carrier density \( N(x) \) is lower than that of the central region. Different carrier density \( N(x) \) will lead to potential difference on the surface, resulting in a high photovoltage in the middle but low near the edge.

The qualitative analysis in theory is consistent with experimental results (figure 3(a)). The relation between the metallic potential \( V(x) \) and the carrier density \( N(x) \) at position \( x \) can be obtained as

\[
V(x) = V_0 + KN_0 \lambda \left[ 2 - e^{-\frac{x}{\lambda}} - e^{-\frac{L-x}{\lambda}} \right]
\]

where \( V_0 \) is the reference potential, and \( K \) is the proportion coefficient. It clearly shows a non-equipotential effect, where the maximum potential \( V_{\text{max}} = V(L/2) \) is obtained at the center and the minimum \( V_{\text{min}} = V(0) = V(L) \) at the edge of the surface.

According to (2), the surface photovoltage and the defined average lateral electric field intensity can be respectively written as

\[
\Delta(V) = KN_0 \lambda \left[ 1 - e^{-\frac{L}{\lambda}} \right]^2
\]

\[
\frac{2\Delta(V)}{L} = KN_0 \frac{2\lambda}{L} \left[ 1 - e^{-\frac{L}{\lambda}} \right]^2
\]

From the previous two equations, it indicates that a longer metal length \( L \) yields a relatively larger surface photovoltage \( \Delta \), but a smaller average lateral electric field \( 2\Delta/V \). This is also consistent with the foregoing discussed experimental results (figures 3(a) and (b)).

As the original density of light-induced electrons \( N_0 \) can be divided into the hot electron flux \( N_1 \) and electron–hole excitation flux \( N_2 \), there are two different mechanisms in the thickness dependence of non-equipotential surface photovoltaic effect. Firstly, as the Ti thickness increases, \( N_1 \) decays with enhanced scattering in the metal within the mean free path. What’s more, the generation possibility of \( N_1 \) also decreases because the light intensity decays exponentially with metal thickness according to Beer–Lambert’s law. Due to that, the photon energy is much higher than Si energy gap, it is expected that \( N_2 \) offers a more contribution than \( N_1 \). Thus, the dependence of surface potential on the thickness could be closely related to the diffusion behaviors in the metal films.

Generally, in bulk metals, electrons can diffuse easily with an infinite diffusion length. It means if there exists electron density difference inside any place of a metal, it will be erased immediately. That is why a
bulk metal is always equipotential as observed in most cases. However, when the thickness of metal film is reduced to nanoscale, according to the Kubo theory [32, 33], the electrons in a nano metal film are no longer as free as they are in a bulk metal. In this case, electrons are hard to diffuse, resulting in a finite and short diffusion length. In consequence, the density difference cannot be erased. That is considered to be the root of the non-equipotential effect in nano metal films. According to the lateral photovoltaic effect in nano metal films, we get \( \lambda(d) = \beta(d - d_0) \), where \( \beta \) is a proportional coefficient and \( d_0 \) is the threshold thickness. Therefore, \( \Delta \) can be written as

\[
\Delta (d) = K N_0 \beta (d - d_0) \left[ 1 - e^{-\frac{d}{2(d - d_0)}} \right]^2
\]

(5)

It tells that a suitable metal thickness is crucial for obtaining an obvious non-equipotential effect. Whether the metal is too thick or too thin, \( \Delta \) will become negligible, indicating an equipotential surface. According to (5), the optimum thickness can be presented as \( d_{opt} = d_0 + \alpha L \), where \( \alpha = 1/2.4 \beta \) is a proportional coefficient. It demonstrates a larger metal length results in a larger optimal metal thickness, which fits well with the experimental observations as shown in figure 5(c).

In addition, based on the previous calculation of bipolar-resistance effect [34], \( \Delta \) can also be presented as

\[
\Delta (p) = K \lambda n_0 \left[ 1 - C \frac{p}{p_0} \right] \left[ 1 - e^{-\frac{L}{\lambda n_0}} \right]^2
\]

(6)

where \( n_0, C(<1) \) and \( \tau \) are three related coefficients. This gives the relationship between surface photovoltage and light power \( p \), which can be also confirmed by the experimental results (figure 3(d)).

According to the experimental results and theoretical analysis mentioned above, the non-equipotential effect observed on the surface of Ti/Si promotes a deep investigation of the charge carriers generation and diffusing behavior. As the non-equipotential surface photovoltaic effect is sensitive to the thickness and size of the metal films, it may promise some novel applications, such as evaluating the thickness and morphology of nanoscale ultra-thin metal films based on potential difference. In addition, with a uniform illumination on the surface of Ti/Si, the high potential in the center and the low on the edge can probably represent two different states of 1 and 0. It may offer a new way to distinguish signals and improve the storage density of optical memory materials. Thus, the surface potential effect may expand some possible application prospects of nanoscale metal–semiconductor systems in optical storage field.

3. Conclusion

In conclusion, we have observed a remarkable surface photovoltaic effect on the surface of nano metal films when they are uniformly illuminated by a light. This effect is characterized by a central-high metallic potential, which is attributed to the boundary effect of the electron diffusion model in nanoscale metal–semiconductor systems. This work reveals a deep understanding of the electron behavior in nano metal films and may propose some applications to multifunctional photoelectric devices.

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ORCID iDs

Shuai Liu https://orcid.org/0000-0002-2584-7801
Hui Wang https://orcid.org/0000-0002-6653-4086

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