Influence of annealing on Fermi-level pinning and current transport at Au-Si and Au-GaAs Interfaces

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The measurements of internal photoemission and photovoltage within the temperature range of 7–300 K have been performed for unannealed and annealed Au/n-Si and Au/n-GaAs samples. From the internal photoemission measurements, it was observed that annealing at different temperatures does not affect the relativity of interfacial Fermi-level pinning to either the conduction band (for Au/GaAs) or the valence band (for Au/Si) but leads to a significant change of the Schottky barrier height. On the other hand, the photovoltage measurements show that the current transport at the metal/semiconductor interfaces is seriously affected by annealing. © *1995 American Institute of Physics.*

The issue of Schottky barrier formation at metal-semiconductor interface has attracted considerable interest for many years and has continued to puzzle the semiconductor physics community.[1–3] As any physical and chemical changes taking place at the interface may affect the properties of Schottky barrier, the study of the influence of annealing on Fermi-level pinning and current transport at the interface may lead to an insight into the mystery of Schottky barrier formation. In fact, it has already been observed that annealing can cause a degradation of the I-V characteristics of Schottky contacts, and such degradation cannot usually be explained simply in terms of a change in Schottky barrier height.[3] In the present study the Schottky barrier height and its temperature dependence in both unannealed and annealed Au/n-Si and Au/n-GaAs Schottky contacts are measured by the internal photoemission technique[4,5] within the temperature range of 7–300 K. This technique is an accurate and direct method of determining the Schottky barrier height, which avoids problems encountered using the I-V technique, such as the influence of recombination current at low temperatures or the degradation of the I-V characteristics due to annealing. As varying the temperature is the simplest way of varying the band gap in semiconductors, measurement of the temperature dependence of the Schottky barrier height can provide useful information on the relativity of the Fermi-level pinning (i.e., whether pinning is relative to conduction or valence bands). Also in this study, the photovoltage measurements are carried out to investigate the problem of current transport, and the result clearly shows that annealing can seriously affect the current transport.

The substrates used in this study are an n-Si (111) wafer with a doping concentration of 1×10^{15} cm^{-3} and an n-GaAs (110) with a doping concentration of 3×10^{15} cm^{-3}. The circular Au/n-Si and Au/n-GaAs Schottky contacts with diameters in the range of 4–6 mm are fabricated by evaporating 150 Å of gold film through a metal mask onto the chemically cleaned surfaces of the semiconductors in a vacuum of $\sim10^{-6}$ mbar. Some of the samples are subsequently annealed at different temperatures in a forming gas atmosphere (80% N_2 and 20% H_2). Prior to the deposition of Au film, low-resistivity ohmic back-contacts are formed by alloying Au-Sb (88:12) pellets on the back of Si substrates and tin pellets on the back of GaAs substrates in a vacuum of $\sim10^{-6}$ mbar.

Both the internal photoemission measurements and the photovoltage measurements are carried out in the HS-4 HELIPLEX® closed-cycle helium refrigeration system with CaF_2 optical windows. The temperature of the samples can be controlled with an accuracy of ±0.2 K in the temperature range of 4–300 K. A monochromatic light beam is delivered by a monochromator (Bentham M300) equipped with appropriate gratings and filters. The relative incident photon flux at each energy is determined by a pyroelectric photodetector. In the internal photoemission measurements the incident beam was modulated by a chopper, and the modulated photocurrent on a loaded resistor is detected by a lock-in amplifier. The usual Fowler plot,[6] i.e., the square root of photocurrent normalized by unit incident photon flux versus photon energy, yields a direct determination of the Schottky barrier height by the extrapolation of the linear portion of the curves to zero photocurrent. In the photovoltage measurements, the "open-circuit" photovoltage is measured by a Keithley electrometer with 10^{14} Ω input impedance, and the "short-circuit" photocurrent is measured with a digital picoammeter (Keithley 485).

Figures 1(a) and 1(b) show, respectively, the Fowler plots at various temperatures for the unannealed Au/n-Si contact and the Au/n-Si contact annealed at 200 °C for 30 min. The intersection of the extrapolation with the energy axis gives the Schottky barrier height values at different temperatures. For both the unannealed and annealed contacts, this intersection simply moves toward higher energy as the temperature decreases indicating an increase of the Schottky barrier height with decreasing temperatures. Figure 2 shows the Schottky barrier heights as a function of temperature in Au/n-Si contacts which are unannealed, annealed at 100 °C for 10 min and annealed at 200 °C for 30 min, respectively. It is evident from Fig. 2 that annealing causes a small increase of the Schottky barrier heights but does not change the temperature dependence of the Schottky barrier heights in the Au/n-Si contacts. The annealing at 100 and 200 °C leads to an increase of Schottky barrier height with ~20 and ~25 meV, respectively. As can be seen in Fig. 2, the temperature dependence of the Schottky barrier heights in both

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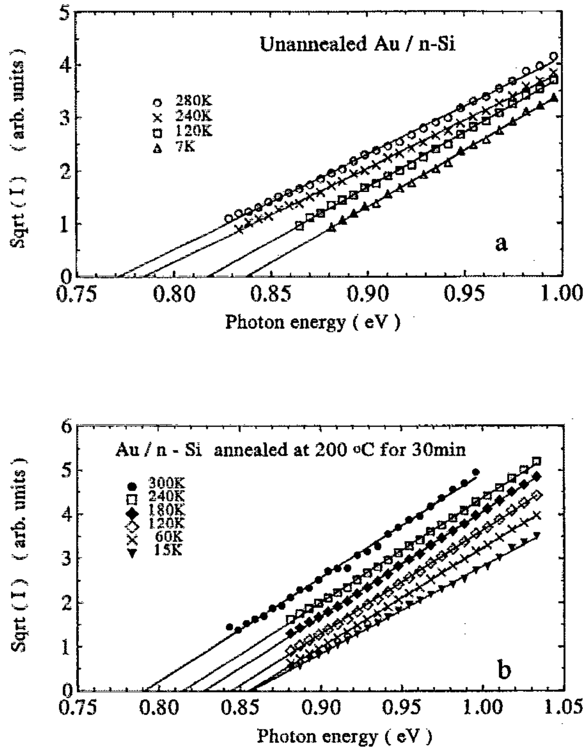

FIG. 1. Square root of the normalized photocurrent in (a) unannealed Au/n-Si contact, and (b) Au/n-Si contact annealed at 200 °C for 30 min.

the unannealed and annealed Au/n-Si contacts is almost identical to that of the indirect band gap in silicon. This implies that the Fermi level at the Au/Si interfaces is pinned relative to the nearest valence-band maximum (VBM) in silicon, and the annealing does not affect the relativity of the Fermi-level pinning to the VBM.

On the other hand, for the unannealed Au/n-GaAs contact, the intersection of the linear extrapolation with the energy axis in the Fowler plots remains 0.890 ± 0.015 eV in the temperature range of 7–300 K. The variation of the Schottky barrier height in this unannealed contact is shown by the

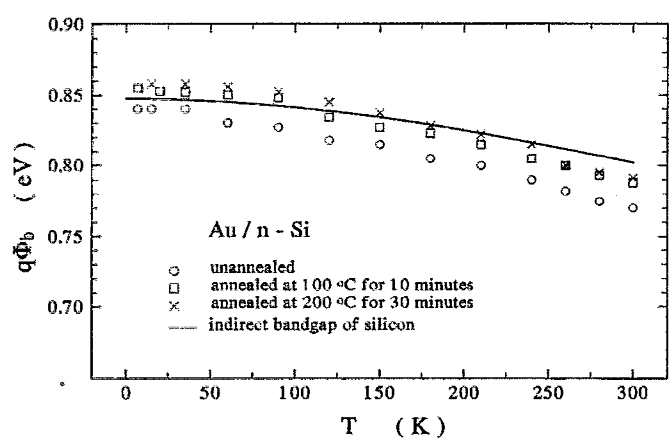

FIG. 2. Annealing effect on the Schottky barrier height and on its temperature dependence in the Au/n-Si contacts. The solid curve shows the temperature dependence of the indirect band gap in silicon.

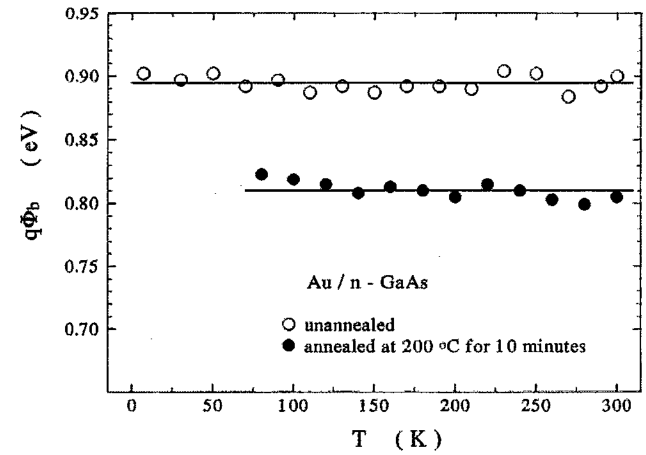

FIG. 3. Annealing effect on the Schottky barrier height and on its temperature dependence in the Au/n-GaAs contacts. The two straight lines are for guiding the eye only.

open circles in Fig. 3. It is evident from this temperature dependence of the Schottky barrier height that the position of the Fermi level at the interface relative to the nearest conduction-band minimum (CBM) in gallium arsenide actually remains unchanged with temperature, implying that the Fermi level is pinned relative to the CBM. For Au/n-GaAs, as shown in Fig. 3, although annealing does not change the temperature dependence of the Schottky barrier heights, it leads to a lower Schottky barrier height. This is in contrast to the case of Au/n-Si in which annealing leads to a higher Schottky barrier height. The annealing at 200 °C for 10 min causes a decrease of the Schottky barrier height by ~80 meV. A similar annealing effect on the Schottky barrier height has been reported, and is associated with the interdiffusion and degradation of Au/GaAs interfaces.[7] It has been observed that the annealing at 250 °C leads to a gold diffusion into the GaAs and a Ga outdiffusion to the surface, and that the Schottky barrier height changes from ~0.9 eV in the unannealed contacts to ~0.7 eV in the contacts annealed at 200–300 °C.[7] It is interesting to note that, although the annealing can cause a degradation of interface and a significant change in barrier height, it does not change the relativity of the Fermi-level pinning at the interface to the CBM.

In order to investigate the influence of annealing on current transport at the metal-semiconductor interface, we have performed measurements of the photovoltage. Detailed descriptions of photovoltage in Schottky contacts have been presented elsewhere.[5,8] In the photovoltage measurements, the thermal-equilibrium condition of the metal/semiconductor system is disturbed by photon excitation. Processes such as thermionic emission over the barrier, tunneling through the barrier, or recombination in the depletion region exist to restore the system to equilibrium. In steady state, a restoring current J due to these processes must balance the photocurrent J_{pc} produced within the depletion region, i.e.,

$$J = J_{pc}, \qquad (1)$$

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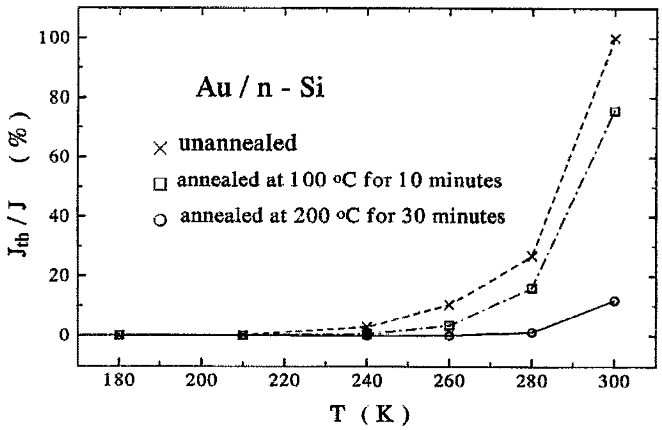

FIG. 4. The influence of annealing on the contribution of the thermionic emission current J_{th} to the total current J in the Au/n-Si contacts.

It is generally believed that the current transport is dominated by thermionic emission and the I-V behavior obeys the thermionic emission theory.[3] However, we show that this idea is true only for the unannealed samples at room temperature, and annealing will cause a departure of current transport from the thermionic emission behavior. This can be seen clearly through the contribution of thermionic emission J_{th} to the restoring current J, i.e., J_{th}/J in the photovoltage measurements. The thermionic emission current is given by[3]

$$J_{th}=A^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right)\left[\exp\left(\frac{qV}{kT}\right)-1\right], \quad (2)$$

where A^* is the Richardson constant, $q\Phi_b$ is the Schottky barrier height, and V is the photovoltage. From Eqs. (1) and (2), J_{th}/J can be written as

$$\frac{J_{th}}{J}=\frac{A^*T^2}{J_{pc}} \exp\left(-\frac{q\Phi_b}{kT}\right)\left[\exp\left(\frac{qV}{kT}\right)-1\right]. \quad (3)$$

In the photovoltage measurements the photovoltage V and the photocurrent J_{pc} are measured. Using the Schottky barrier heights which are determined from the internal photoemission measurements (shown in Fig. 2), we can calculate J_h/J with Eq. (3). The variation of J_{th}/J with temperature for both the unannealed and annealed Au/n-Si contacts is shown in Fig. 4. At room temperature, J_{th}/J is almost equal to 100% for the unannealed sample, indicating that the current transport is dominated by thermionic emission at room temperature; however, J_{th}/J decreases to be 76% and 13% for the samples annealed at 100 °C for 10 min and at 200 °C for 30 min, respectively. After a careful check, we find that the decrease of J_{th}/J cannot be attributed to the change of Schottky barrier height. In the unannealed sample, J_{th}/J decreases as temperature decreases, and the contribution of thermionic emission is insignificant at low temperatures. In previous studies[5] we have shown that, for the unannealed sample with a doping concentration of 1×10^{15} cm^{-3}, the contribution of tunneling is insignificant and the current transport at low temperatures is dominated by recombination current. As can be seen in Fig. 4, the temperature dependence of J_{th}/J in the annealed samples is similar to that in the unannealed sample, indicating that the departure of current transport from thermionic emission in the annealed samples is also due to the influence of the contribution of recombination current. We therefore conclude that the annealing can enhance the contribution of recombination current. Gold has been known to be a fast diffusing species in Si and GaAs and produces deep levels[7,9] which can be efficient recombination centers. Therefore, the enhancement of recombination current is probably due to the introduction of these efficient recombination centers in the depletion region by annealing. Obviously, the reduction of J_{th}/J due to annealing can explain the generally observed degradation of I-V characteristics caused by annealing.

In conclusion, the influence of annealing on Fermi-level pinning and current transport at Au/n-Si and Au/n-GaAs interfaces has been investigated by internal photoemission and photovoltage measurements. Annealing leads to a change of Schottky barrier heights but it does not affect the relativity of Fermi-level pinning to either VBM (for Au/n-Si) or CBM (for Au/n-GaAs). The annealing also has a strong influence on current transport, causing a departure of current transport from the thermionic emission behavior. Such a departure is attributed to the enhancement of recombination current caused by annealing.

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