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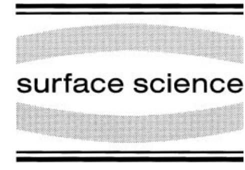

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Photoconductivity of the Si(111)-7 × 7 and $\sqrt{3}\times\sqrt{3}$-Ag surfaces

Chun-Sheng Jiang [a,*], Shuji Hasegawa [a,b]

[a] *Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[b] *Core Research for Evolutional Science and Technology (CREST), The Japan Science and Technology Corporation (JST), Kawaguchi Center Building, Hon-cho 4-1-8, Kawaguchi, Saitama 332-0012, Japan*

Abstract

The photoconductivity of a Si(111) wafer was found to strongly depend on the surface superstructures on it. Positive photoconductivities were measured on the clean 7 × 7 surface with photon energies larger than the band gap energy, which was attributed to the creation of excess electron-hole pairs in the bulk. On the $\sqrt{3}\times\sqrt{3}$-Ag surface, however, negative photoconductivities were measured with light of the same energy range. This phenomenon was qualitatively explained as a result of a reduction of the conduction electrons in a surface-state band, which was due to an enhanced recombination rate between the surface-state electrons and the excess holes created in the surface space-charge layer by illumination. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photoconductivity; Silicon; Surface electrical transport; Surface electronic phenomena; Surface structure

1. Introduction

In-depth understanding of physical phenomena related to photoconductivity in semiconductor bulks has been attempted for over 100 years (for reviews, see Refs. [1,2]. The phenomena include carrier excitation by photons, relaxation and recombination of free carriers, and effects of defects, etc. In most cases, under equilibrium states between the excitation and recombination, excess electron-hole pairs are created, and positive photoconductivities are measured. That is, the conductivities of bulk semiconductors become larger under illumination of light than in the dark. Despite the understanding of photoconductivity in the bulk, photoconductivity on surfaces is less understood, especially on atomically ordered surfaces investigated in ultrahigh vacuum (UHV)[3].

For certain surfaces such as the Si(111)-7 × 7 and $\sqrt{3}\times\sqrt{3}$-Ag, the atomic arrangements[4–10] and electronic structures [11–19] are now well understood. Then, a simple question arises: What is the relationship between surface electronic states and photoconductivity? Is photoconductivity affected by the surface electronic states and the surface space-charge layer? In this paper, we report the results of photoconductivity measurements on the Si(111)-7 × 7 and $\sqrt{3}\times\sqrt{3}$-Ag surfaces in UHV. On the clean 7 × 7, a normal positive photoconductivity was measured which was attributed to the creation of excess electron-hole pairs in bulk. What was surprising in our measurements

* Corresponding author. Present address: Surface and Interface Laboratory, The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01, Japan. Fax: +81-48-462-4656
E-mail address: jiang@postman.riken.go.jp (Chun-Sheng Jiang)

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was that on the $\sqrt{3}\times\sqrt{3}$-Ag surface, a negative photoconductivity was measured even when light excited excess electron-hole pairs. We tentatively explained this strange phenomenon in terms of the reduction of mobile electrons [15–17,20] in a surface-state band of the $\sqrt{3}\times\sqrt{3}$-Ag surface because of an enhanced recombination rate of the surface-state electrons with the excess holes created in the sub-surface region under illumination.

2. Experiments

A Si(111) wafer (n-type, resistivity = 50 Ω cm) of $40\times5\times0.4$ mm^3 in size was cleaned in UHV by flashing at 1200°C and annealing at temperatures around 750°C with passing a direct current through the wafer. The $\sqrt{3}\times\sqrt{3}$-Ag structure was prepared at a substrate temperature of 510°C by depositing Ag at a rate of 0.4 ML/min. The amount deposited was calibrated with a reference of 1 ML Ag for completing the $\sqrt{3}\times\sqrt{3}$-Ag phase [6–8]. During sample preparation, reflection high-energy electron diffraction (RHEED) was used to monitor structural changes.

Fig. 1 schematically shows the equipment for photoconductivity measurements. To measure the conductivity parallel to the sample surface, four probes (Ta wires) were set linearly on the back of the wafer to avoid direct irradiation of light at the probe–sample contact points. This is because such an irradiation creates voltage noise due to the photodiode-like effect at the contacts. A constant current was made to flow through the outer pair of probes, and voltage signals were picked up by the inner pair. Then, the conductivity of the sample in between the inner pair was measured. In contrast to the conventional setup employed in our previous work[20–30] where the probes were set on the front surface, setting the probes on the rear face made no difference to the measurement, since they measured the electric potential gradient along the sample.

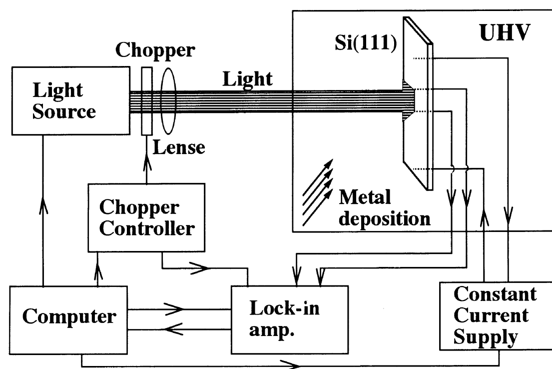

Fig. 1. A schematic diagram of the experimental set-up for measuring photoconductivity in UHV.

Light was irradiated onto the sample surface at normal incidence. Monochromatic light with photon energies between 0.75 and 1.6 eV or 1.6 and 3.0 eV at constant power was produced from a Xe or a halogen lamp, respectively, using a monochromator. The power was maintained at a constant value by an attenuator which was controlled by a feedback from a light power monitor. The light output was conducted through an optical fiber from the light source unit, and focused on the sample though a view port on the UHV chamber. The diameter of the irradiated area on the sample surface was 5 mm, which was almost the same as the width of the sample and the distance between the voltage probes. The light was chopped and its frequency (400 Hz) was delivered to a lock-in amplifier as reference. Amplitudes and phases of the voltage signals were measured by a two-phase lock-in amplifier. In the case of the 0° or 180° phase, the measured voltages were positive or negative, corresponding to negative or positive photoconductivity, respectively. The light source, the lock-in amplifier, and the chopper were controlled by a personal computer.

3. Results and discussions

Fig. 2a shows the change in measured voltage between the inner probes induced by illumination on the Si(111)-7×7 and $\sqrt{3}\times\sqrt{3}$-Ag surfaces as a function of the irradiated photon energy with a constant light power of 35 μW and a measuring current of 100 μA. As shown in the right ordinate of the graph, the voltage corresponds to the change in resistance caused by illumination, in comparison

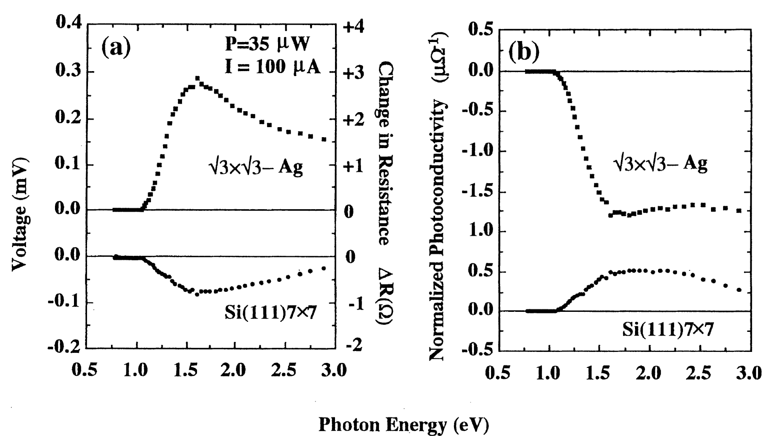

Fig. 2. (a) Voltages between the inner pair of the probes induced by light illumination measured on the Si(111)-7 × 7 and $\sqrt{3}\times\sqrt{3}$-Ag surface structures. The corresponding changes in resistance are indicated on the right ordinate. (b) Photoconductivity calculated from the resistance change in (a), normalized by a reference at a photon energy of 1.65 eV with a photon flux of 1.3×10^{14} photons/s for compensating the different amounts of photons at various photon energies with the same light power of 35 μW.

with in dark. Fig. 2b shows the change in the normalized photoconductivity $\Delta\sigma$ calculated from the measured resistance changes in Fig. 2a using $\Delta\sigma = N(h\nu)\times\Delta R/R_0^2$, where ΔR and R_0 are the change of resistance shown in Fig. 2a and the dark resistance, respectively. $N(h\nu) = h\nu/1.65$ ($h\nu$ is the photon energy) is a normalization coefficient for compensating different amounts of photons with various photon energies at the same light power, in a reference at $h\nu = 1.65$ eV, which corresponds to 1.3×10^{14} photons/s.

The photoconductivity begins to change above a photon energy of around 1.1 eV (Fig. 2b) for both surfaces, which corresponds to the fundamental band gap. For the 7 × 7 surface, the photoconductivity increases with the photon energy, and saturates at around 1.6 eV. Above 2.3 eV, it decreases slightly. For the $\sqrt{3}\times\sqrt{3}$-Ag surface, a negative photoconductivity is measured. The conductivity decreases from 1.1 eV, and saturates around at 1.6 eV. Above 1.8 eV, it increases slightly. In this way, the photoconductivities were found to depend decisively on the surface structures. The maximum and minimum values of the normalized photoconductivity at 1.6 eV for the 7 × 7 and $\sqrt{3}\times\sqrt{3}$-Ag surfaces are +0.5 and $-1.8\ \mu\Omega^{-1}$, respectively.

Since the observed photoconductivity of both surfaces appears only at photon energies larger than the band gap of the bulk states, we can say that it is not related directly to the photoexcitations in the surface states; the photoexcitation in the bulk should be responsible for the measured photoconductivity. This is because the respective surface structures have different surface electronic states within the band gap[11–19], so the threshold photon energies for conductance changes should be different from each other if the surface states play major roles. Then, two types of electrical conduction should be considered to interpret our results: conduction through the bulk (especially through the surface space-charge layer) and that through the surface-state bands. Do the surface structures affect the photoexcitation processes in the subsurface region in the bulk (surface space-charge layer)? Is the electrical conduction through the two-dimensional surface-state bands affected by the photoexcitation in the bulk?

Fig. 3a, b shows schematically the band diagrams for both surface structures without light irradiation. For the 7 × 7 surface, the surface Fermi level (E_F) is known to be pinned at the surface state S_1 (corresponding to the adatoms' dangling-bond state) around the middle of the band gap[11,31]. For an n-type sample, the surface space-charge layer is electron-depleted. The electric field in the layer, due to the dipoles formed by ionized dopants and excess negative charges

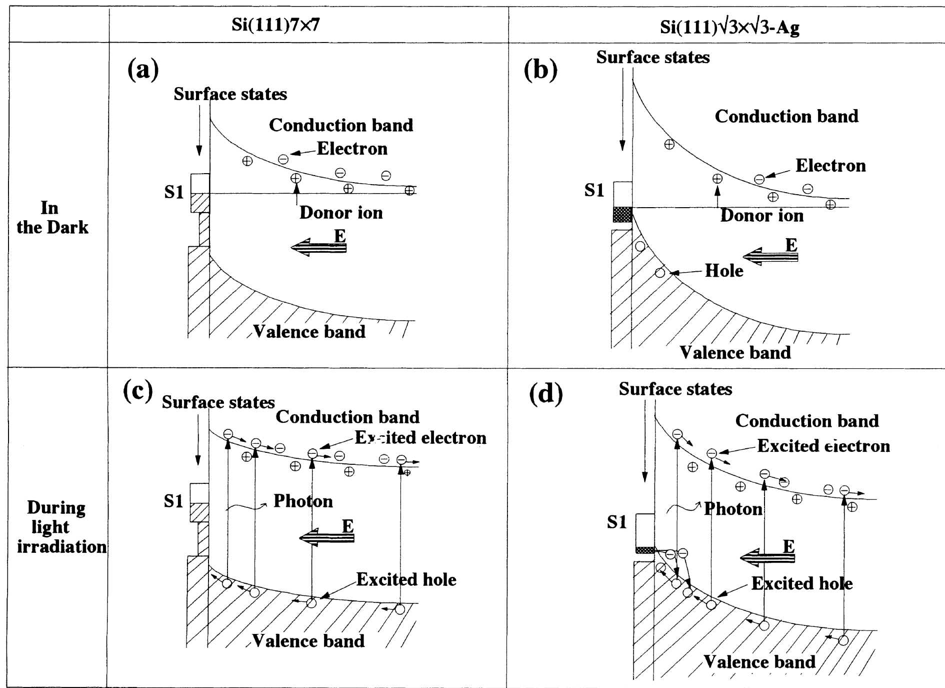

Fig. 3. Schematic band diagrams for the Si(111)-7×7 (left-hand column) and the $\sqrt{3}\times\sqrt{3}$-Ag (right-hand column) surfaces in the dark (upper row) and during light illumination (lower row).

trapped at the S_1 state, points to the surface from the bulk interior. On the other hand, for the $\sqrt{3}\times\sqrt{3}$-Ag surface, since the surface E_F is known to be pinned at the surface state S_1 (originating from an antibonding state between Ag and Si atoms) close to the top of the valence band[15–17,32], the space-charge layer is an inversion layer. The electric field in the layer points from the bulk to the surface again, but it is stronger than that under the 7×7 surface. With absorption of photons whose energy is larger than the band gap, electron-hole pairs are excited (Fig. 3c and d). Since the period (2.5 ms) of the chopped light is much longer than the lifetime of the electron-hole pairs at room temperature (~μs [33,34]), excess pairs with a constant density are created in a steady state. This is why positive photoconductivity for the 7×7 surface is observed at photon energies larger than the band gap. The photoexcited electrons and holes in the surface space-charge layer diffuse toward the bulk interior and toward the surface, respectively, by the electric field, making the bands flatter (surface photovoltaic effect). Surface photovoltage was actually detected on the 7 ×7 surface by Hammers and co-workers [35–39].

We estimate the photoconductivity for the 7×7 structure only by taking the excitation in the bulk into consideration. The increase in conductivity $\Delta\sigma$ due to illumination is given by:

$$\Delta\sigma = \frac{1}{R} - \frac{1}{R_0} = \frac{w}{l}\int_0^d \Delta\sigma(z)\mathrm{d}z$$

$$= \frac{we(\mu_e+\mu_h)}{l}\int_0^d \Delta n(z)\mathrm{d}z,$$

where l and w are the length and the width of the measured surface area, d is the wafer thickness, $\Delta\sigma(z)$ is the distribution of the photoconductivity in the depth direction, and μ_e and μ_h are the mobilities of electrons and holes, respectively.

$\Delta n(z)$ is the photoexcited electron (hole) density at depth z beneath the surface, which is expressed as

$$\Delta n(z)=\frac{\tau}{wl}\frac{\alpha I(z)}{h\nu},$$

where τ and α are the lifetime of the electron-hole pairs and the absorption coefficient of light, respectively. Since the light intensity $I(z)$ at depth z is given by $I(z)=I_0\,e^{-\alpha z}$ and the upper limit d of the integral in the above equation can be approximated to be infinite, we get

$$\Delta\sigma=\frac{\tau(\mu_e+\mu_h)}{l^2}\frac{I_0}{h\nu}e\approx 0.5\ \mu\Omega^{-1},$$

where the intensity of the incident light $I_0=35$ mW, $\tau=3\times10^{-6}$ s [33,34], $\mu_e=1330$ cm^2/Vs, $\mu_h=500$ mm^2/Vs, $l=0.5$ mm, and $h\nu=1.6$ eV. The photoconductivity estimated in this way is of the same order as the measured value in Fig. 2b.

Now we discuss the $\sqrt{3}\times\sqrt{3}$-Ag surface. The surface photovoltaic effect is again expected on this surface because of the steep band bending beneath the surface (Fig. 3b). Then, the photoexcited holes diffuse toward the surface, making the bands flatter (see Fig. 3d) and, as a result, the holes that accumulate beneath the surface become denser than that in the dark. In our previous work [20], the sheet conductance of the $\sqrt{3}\times\sqrt{3}$-Ag surface was measured to be higher than that of the 7×7 surface by 115 $\mu\Omega^{-1}$, which was suggested to be due to the conduction through the two-dimensional surface-state band S_1 of the $\sqrt{3}\times\sqrt{3}$-Ag surface, as well as the holes in the surface space-charge layer (accumulation for the p-type sample). Furthermore, adatoms adsorbed on top of the $\sqrt{3}\times\sqrt{3}$-Ag surface donate electrons into the S_1 band, resulting in an enhanced surface conductance[30,40]. Such adatoms (called 'adatom gas phase') with low density seem to always exist on top of the surface in the thermodynamic equilibrium state [41]. The doped electrons in the surface-state band S_1 are mobile due to their large dispersion [15–17], so that they contribute to the electrical conduction. As mentioned above, the hole density in the subsurface region becomes denser under light irradiation than in the dark. This will enhance the recombination probability of the S_1 electrons with the holes nearby. Some of the conduction electrons in the S_1 band vanish, resulting in a decrease in the conductance through the S_1 band. Since the surface conductivity (115 $\mu\Omega^{-1}$) is much larger than the measured positive photoconductivity (0.5 $\mu\Omega^{-1}$ for the 7×7 case), in the light irradiation, the decrease in surface conductivity is possibly larger than the increase in bulk conductivity, resulting in the measured negative photoconductivity for the $\sqrt{3}\times\sqrt{3}$-Ag surface. For the 7×7 surface, on the other hand, since the electron mobility in the dangling-bond state S_1 should be small because of its negligible band dispersion [11], the conductance through the surface state should be negligible. Therefore, even though the S_1 electrons vanish by combining with the holes created in the subsurface region, this will not significantly affect the conductivity. Thus only the conductance increase in bulk is directly detected. In order to confirm our guesses, photovoltage measurements such as those in Refs. [35–39] and photoemission spectroscopy under light illumination with different intensities will be helpful.

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