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The role of the surface phases in surface conductivity

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Abstract

The surface conductivity of the samples with Au/Si(100), Na/Si(100) and H/Si(100) surface phases was measured in ultra-high vacuum by four-point probe method at RT. We have found that difference in surface conductivity of the silicon substrate with surface phase and clean Si(100)2×1 surface is $(6.0\pm1.9)\times10^{-5}\ \Omega^{-1}\square$ for $c(8\times2)$-Au, $(11.1\pm0.8)\times10^{-5}\ \Omega^{-1}\square$ for $\sqrt{26}\times3$-Au and $-(1.5\pm0.8)\times10^{-5}\ \Omega^{-1}\square$ for 3×2-Na surface phase. These variations of surface conductivity are estimated to originate, in general, from the formation of the surface phases. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Surface phases; Surface conductivity; Silicon substrate

1. Introduction

The processes at the surface (like those in the bulk) are directed towards the establishment of an equilibrium state of the system. This often leads to the formation of surface phase. Though a large number of publications have been devoted to the above subject [1], it is not safe to say the term ''surface phase'' is commonly used in surface science literature since other terms like ''surface superstructures'', ''reconstructions'', ''two-dimensional structures'', etc. are also used as synonyms of what we call surface phases. This situation is believed to result from the fact that surface science is currently a rapidly developing branch of materials science and still far from the status of the ''classical'' science with its well-adopted system of definitions, concepts, and terminology. It is hazardous to offer any new generalization, so we do not pretend to give a strict definition but rather try to explain the meaning we attribute to the term ''surface phase''. We consider surface phases as extremely thin layer in thermodynamic equilibrium with the bulk (with the layer thickness of the order of monatomic layer) whose composition, structures, and properties definitely differ from those of the corresponding planes of bulk (silicon), bulk adsorbate, as well as bulk adsorbate-silicon compound if available. In other words, the surface phase is a specific near-surface material with its own characteristics. Surface phase can be formed either by the same atoms as the bulk or by both substrate atoms and foreign atoms at the surface. The structures of the surface phases are determined by the interactions of the atoms in the surface phase with each other and with substrate atoms as well as by the interaction between the substrate atoms. Hence, from transport properties viewpoint, the surface phase acts as adding conductivity channel and the current passing through the sample covered by

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the surface phase is divided due to the formation of two conducting channels. These are ''bulk'' and ''surface phase'' channels. Surface phases may have single-crystalline, polycrystalline or amorphous structures depending on preparation conditions. One should distinguish between foreign atoms included in the surface phase (''in phase'' atoms) and atoms in excess with respect to the surface phase (''on phase'' atoms). ''In phase'' atoms change the valence bond of Si, strongly bonded with Si substrate. The presence of ''on phase'' atoms has negligible effect on the electronic structures of the system. These atoms are less bonded with substrate. This difference determines the nature of all surface processes and will take into account the surface processes explanations.

The ordered surface phases formed by adsorbate deposition onto the atomically clean semiconductor surface has been studied for more than 30 years. However, their influence on the transport properties have only recently been investigated by means of conductivity and Hall effect measurements carried out in ultra high vacuum. The correlation between surface superstructure and electrical surface conductance is the prime object of these experiments. Starting with the work of Bäuerle et al. [2], the electrical properties of silicon surface has been an object of investigation, which are of much current interest not only from the scientist's viewpoint but also because of the technological applications. Tsukanov et al. [3] found that the submonolayer Au deposition onto RT Si substrates with (100) and (111) orientation leads to decreasing surface conductivity due to the destruction of the surface phase conductivity channel.

In addition, the following reasons affect the value of the surface conductivity.

Surface space-charge layer. Excess charge trapped in the states of the surface phase causes band-bending below it, resulting in changes in carrier concentrations in the space-charge layer, whose width reaches several microns in a lightly doped semiconductor substrate. Thus, the electronic states of each surface superstructure can govern the electrical conductivity through the layer (for example, Si(111)5 × 2-Au surface phase [6]).

Surface roughness. The diffuse scattering of conducting electrons at a rough surface has a considerable contribution to the conductivity of thin films, which is well known as the classical size effect [4].

Conductive islands grown on the surface. Islands are conductive so that the electrical conduction can be set above threshold coverage for percolation paths corresponding to the coalescence among the islands.

Metastable two-dimensional gas phase. If deposited ''on phase'' adatoms are highly mobile (for example, Ag atoms on Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface phase [5]), then they generate a two-dimensional gas phase and due to it they can significantly change the conductivity in the surface region.

For the samples with the same conditions as above the surface conductivity is determined by the difference in conductivity of the surface phase on silicon. At the destruction of the surface phase the surface conductivity must be decreased. The surface phases due to own electrical properties may increase or decrease surface conductivity compared with the silicon surface phase. The present work demonstrates this case.

2. Experimental

Experiments were carried out in an ultra-high vacuum chamber with a base pressure of 2×10^{-10} Torr. A Si(100) wafers (n-type, resistivity = 50 Ω cm) with $20\times5\times0.45$ mm^3 were cleaned in situ by direct Joule heating to 1200°C for several minutes. The cleaned samples displayed the low energy electron diffraction (LEED) patterns characteristic of the clean surface, i.e. Si(100)2 × 1. The Au/Si(100) surface structures were prepared by Au deposition from an Au-coated tungsten filament at a rate of about 0.5 ML/min (1 monolayer (ML) equals 6.8×10^{14} atoms/cm^2 for Si(100), the site density for unreconstructed Si surface). The substrate temperature during Au deposition was about 850°C. Na was deposited at a rate of about 0.2 ML/min from thermal cell onto the sample held at temperature of about 200°C.

For hydrogen exposure, H_2 gas was admitted through a leak valve. A 1800°C tungsten filament was used to dissociate molecular hydrogen. The exposures were conducted with the specimen facing the filament and by backfilling the chamber with H_2 at 5×10^{-6} Torr. Since the arrival rate of atomic hydrogen is unknown but proportional to the molecular hydrogen pressure, the dose of molecular hydro-

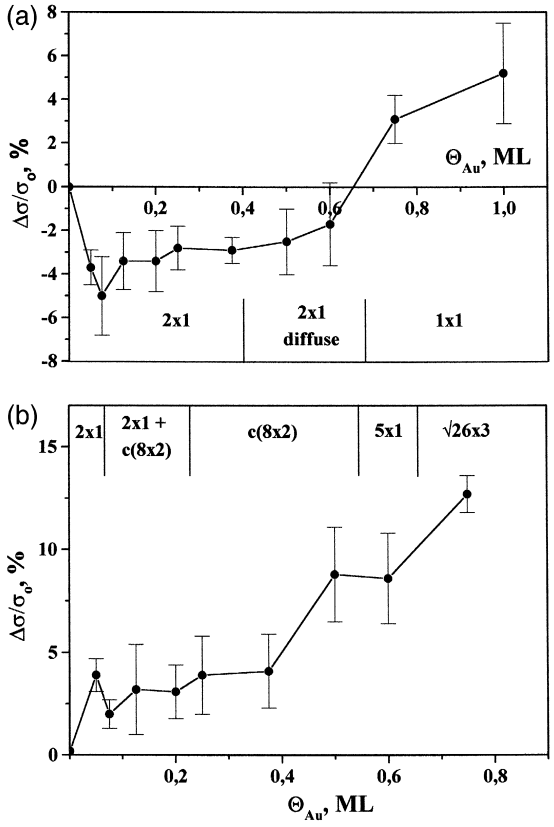

Fig. 1. The surface conductivity changes of Au/Si(100) submonolayer system: (a) at Au deposition at RT; (b) after annealing at 850°C.

gen is specified, expressed in langmuir ($1\ \mathrm{L} = 1 \times 10^{-6}$ Torr s).

For the in situ measurements of surface conductivity parallel to the silicon surface a four-point probe method with direct current was used. The ohmic conditions of electrical contacts between the substrate and the W electrodes, whose spacing was about 1.3 mm, were confirmed by observing a linear relation between voltage signal and electric current in the range of 0–100 μA. After surface structure preparation the sample was cooled down to RT during 1 h to attain a stable conductance. Surface conductivity is defined as $\sigma_s = \sigma \times d = G \times I/V\ \Omega^{-1}\ \square$, where $G = 0.3101$ is dimensional coefficient [7] and d is the thickness of the wafer.

The measured surface conductivity has several components, the main ones are the conductivity through the bulk Si and that through the surface phase. At the surface phase formation the bulk component of the conductivity is equal to the one for the clean Si(100) surface. We have measured the excess surface conductivity appearing because of surface reconstruction due to the formation of the surface phase. Therefore, the surface conductivity we determined as

$$\Delta\sigma_s = \sigma_s(\mathrm{sp}) - \sigma_s(2\times 1)[\,\Omega^{-1}\,\square\,],$$

where $\sigma_s(\mathrm{sp})$ is sample conductivity with surface phase and $\sigma_s(2\times 1)$ is one with clean Si(100)2×1 surface, respectively.

3. Results and discussion

Fig. 1 shows the conductivity changes in the Au/Si(100) system after Au deposition at RT (a) and after sample's annealing at 850°C (b). The regions of surface structures existence observed by LEED are indicated on this figure. During Au deposition at RT on Si(100) surface a disordered film is formed [8]. In the first time an abrupt decrease of reflection intensity and background intensification in the LEED pattern is registered and then after gold deposition the LEED images show a diffuse 2×1 pattern. After 0.6 ML Au deposition a 1×1 pattern is observed. As 2×1 SP is weakened therefore the SP is destroyed and the ''SP'' conductivity channel disappears. In this case surface conductivity decreases for this structure in comparison with the clean substrate. By increasing the Au coverage further when it is about 0.5 ML, surface conductivity begins to increase. We propose that in this case a metal film was formed on the surface [8].

After annealing of the samples with Au films with coverage less then 1 ML deposited at RT, SPs Si(100)-Au are formed. Instead surface conductivity

Table 1
The surface conductivity of Si(100)-Au and Si(100)-Na surface phases

Surface phase	Coverage (ML)	$\sigma_s(\mathrm{sp}) - \sigma_s(2\times 1)$, $\times 10^{-6}\ \Omega^{-1}\ \square$
Si(100)$c(8\times 2)$-Au	0.5	60 ± 19
Si(100)$\sqrt{}$26x3-Au	1	111 ± 8
Si(100)3×2-Na	0.35	$-(15 \pm 8)$

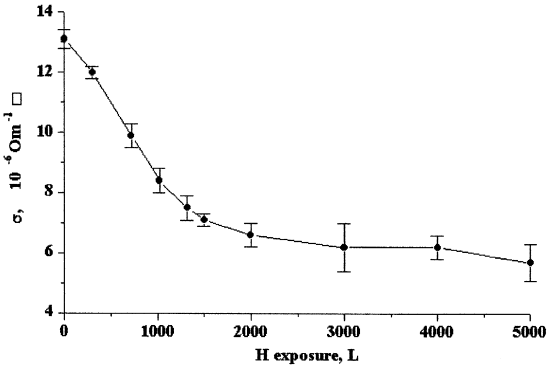

Fig. 2. The conductivity changes during the atomic hydrogen exposure onto Si(100)2×1 surface.

channels formed by Si(100)2 × 1 SP surface conductivity channels are formed again by Si(100)-Au SPs. In the last case as shown in Fig. 1(b) the surface conductivity for the Au/Si(100) system is distinctly higher than that for the SP of the clean Si(100)2 × 1.

The values of conductivity, calculated from experimental data, are shown in Table 1. We propose that surface conductivity increase is proportional to the Au coverage of the Au/Si(100) surface phase. The atom density in Si(100)$\sqrt{26} \times 3$-Au surface phase is higher by a factor of two than that for Si(100)$c(8 \times 2)$-Au ($\theta_{Au} = 0.5$ ML for $c(8 \times 2)$ and $\theta_{Au} = 1$ ML for $\sqrt{26} \times 3$ superstructure [9]) and, hence, we see the double increase of surface phase contribution to the surface conductivity.

Notice that conductivity through the additional channel may be more or less comparable with the conductivity of the clean silicon substrate with Si(100)2 × 1 SP. The last case is realized for the Na/Si(100) system (see Table 1). Formation of the 3 × 2-Na surface phase (Na coverage is about 1/3 ML[10]) reduces the surface conductivity. Interaction between Na atoms is weak and Si(100)-Na SP is not metallized at low coverage (less then 1 ML [11,12]).

If the Si(100) surface is exposed to atomic hydrogen at RT the surface conductivity is different from Au/Si(100) and Na/Si(100) systems behavior. It is well known that atomic hydrogen saturates dangling bonds of the silicon surface [13] leading to the destruction of the Si(100)2 × 1 SP and forming monohydride Si(100)2 × 1-H surface phase. We observed the strong decrease of the surface conductivity (Fig. 2) due to the disappearance of the conductivity channel formed by Si(100)2 × 1 Si. The additional factor affecting the conductivity decrease is the surface etching by atomic hydrogen [14] and, therefore, surface roughness enhances the carriers scattering [4].

The obtained results were qualitatively confirmed for p-type silicon samples.

4. Conclusion

We would like to emphasize some important results of our investigation. Formation of the surface phases have different influence to Si(100) surface conductivity. Si(100)-Au surface phase increases the surface conductivity, Si(100)3 × 2-Na and Si(100)2 × 1-H surface phase decrease it. Surface phases form the conductivity channel on Si(100) surface. Properties of this channel depend on composition and structure ordering of the surface phases.

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