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Surface Conductivity of Submonolayer Au/Si System

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Using the four-point probe method, we studied *in situ* the surface conductivity of submonolayer Au/Si(100) and Au/Si(111) system. Electrical measurements showed that surface phases act as an additional conductivity channel. The value of conductivity of this channel depends on the structural and electronic properties of the surface phases. Destruction of the surface phase of atomically clean silicon by adsorbed Au atoms reduces the conductance of the substrate.

1. Introduction

Recently, a number of papers appeared concerning the transport properties of surface superstructures formed by submonolayer adsorbate deposition onto silicon [1, 2, 3, 4, 5]. The obtained results indicate the decisive role of surface phases in electrical properties.

It is obvious today that it is necessary to distinguish between the terms "surface" and "surface phase". Surface phase is the ultra-thin layer on the surface that is in thermodynamic equilibrium with the bulk with its own electronic and geometrical structure and properties [6]. According to this approach the surface phase is considered as a promising material contacting the bulk. Hence, the current passing through the sample covered by the surface phase is divided due to the formation of two conducting channels. These are "bulk" and "surface phase" channels.

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

1) Surface space-charge layer. Excess charge trapped in the states of the surface phase causes band-bending below it, resulting in the 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

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surface superstructure can strongly affect the electrical conductivity through the layer.

2) 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 [7].

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

4) Metastable two-dimensional gas phase. If deposited adatoms are highly mobile (for example, Ag atoms in Si(111)$\sqrt{3} \times \sqrt{3}$-Ag surface phase [8]), then they generate a two-dimensional gas phase and hence can significantly change the conductivity in the surface region.

For the samples with the same surface space-charge layer and surface roughness the surface conductivity is determined by the difference in the conductivities of the surface phase on silicon. Destruction of the surface phase should reduce the surface conductivity, as demonstrated in the present study.

2. Experimental procedures

Experiments were carried out in an ultra-high vacuum (UHV) chamber. Si wafers ($n-$type Si(100) 50 $Ohm \cdot cm$, $p-$type Si(111) 20 $Ohm \cdot cm$) were cleaned *in situ* by direct Joel heating to 1200°C for several minutes. Surface superstructure was controlled by reflection high-energy electron diffraction (for Si(111) samples) and low-energy electron diffraction (for Si(100) samples). The Si-Au surface structures were made by gold deposition with a rate of $0.2 \div 0.4$ ML/min (1 monolayer (ML) equals $6.8 \cdot 10^{14} cm^{-2}$ for Si(100) and $7.8 \cdot 10^{14} cm^{-2}$ for Si(111) surface). For the preparation of ordered Si-Au surface phases, gold deposition was made at the substrate temperatures of 800°C (for Si(100)$c(8 \times 2)$-Au and Si(100)$\sqrt{26} \times 3$-Au surface phases) and 680°C (for Si(111)5×2-Au surface phase).

The four-point probe method with a direct current was used for the *in situ* measurements of the surface conductivity parallel to the silicon surface. Before the conductivity measurements, the quality of the electrical contact between the substrate and the electrodes was confirmed by observing a linear relation between voltage signals and electrical current in the 0–100 μA range. Because the heat conduction was very slow in UHV environment, it took more than 1 hour for the sample to cool down to RT to attain a stable resistance after the surface structures were prepared.

Since the "bulk" conductivity is the same, we defined the conductivity difference of the sample with the Si-Au surface phase and the silicon sample with the Si(100)2 × 1 surface phase as

$$\Delta\sigma = \sigma_s(sp) - \sigma_s(a.c.\ Si\ surface)\ [Ohm^{-1} \cdot square],$$

where σ_{sp} is the conductivity of the with Si-Au surface phase and σ_s (a.c. Si surface) is the conductivity of the sample with atomically clean silicon surface (Si(100)2 × 1 or Si(111)7 × 7 surfaces). This value was measured in our experiments.

3. Results and discussion

In the present work, our primary attention was given to the study of the surface conductivity of Au/Si(100) and Au/Si(111) submonolayer systems formed both at room temperature and after annealing at 800°C and 680°C for Si(100) and Si(111) substrates, respectively.

Fig.1 shows the change of silicon sample resistivity during submonolayer gold deposition at RT. It was shown that during gold deposition onto both Si(111) and Si(100) at a coverage less than 0.1 *ML* the surface resistivity increases noticeably compared to atomically clean silicon surface with Si(111)7 × 7 and Si(100)2 × 1 surface phases. At further gold deposition at a coverage from 0.1 to 0.5÷0.7 *ML* for Si(111) and for Si(100) the change of the surface resistivity is weak, and at further gold deposition the surface resistivity is decreased rapidly.

These phenomena may be interpreted by destruction of the surface phases Si(111)7 × 7 (Fig. 1a) or Si(100)2 × 1 (Fig.1b) at gold coverage about 0.1 *ML*. Electron diffraction patterns revealed the gradual degradation of the ordering of the surface structures. Therefore, in that case, the surface conductivity channel formed by the surface phase of clean silicon is destroyed resulting in the enhancement of surface resistivity.

In the coverage range from 0.1 to 0.5÷0.7 *ML* of Au for Si(111) and for Si(100), none of gold surface phases is formed on the surface, therefore, in this range the surface resistivity is not changed significantly.

Above 0.5 *ML* gold coverage, the reduction of surface resistivity is observed. According to UHV-SEM (secondary electron microscopy) observations [9], small islands of a few nanometers in diameter appear, and then begin to coalesce with increasing Au coverage, although it is not clear whether the islands are so conductive that the electrical conduction can be set above the threshold coverage for percolation paths corresponding to the coalescence among the islands. In fact, according to the measurements of the Si$-2p$ core-level shifts using XPS (X-ray photoelectron spectroscopy) during this deposition, the Fermi energy E_F does not shift significantly, thus remaining in the depleted condition at the surface space-charge layer [10, 11]. Therefore the reduction of the surface

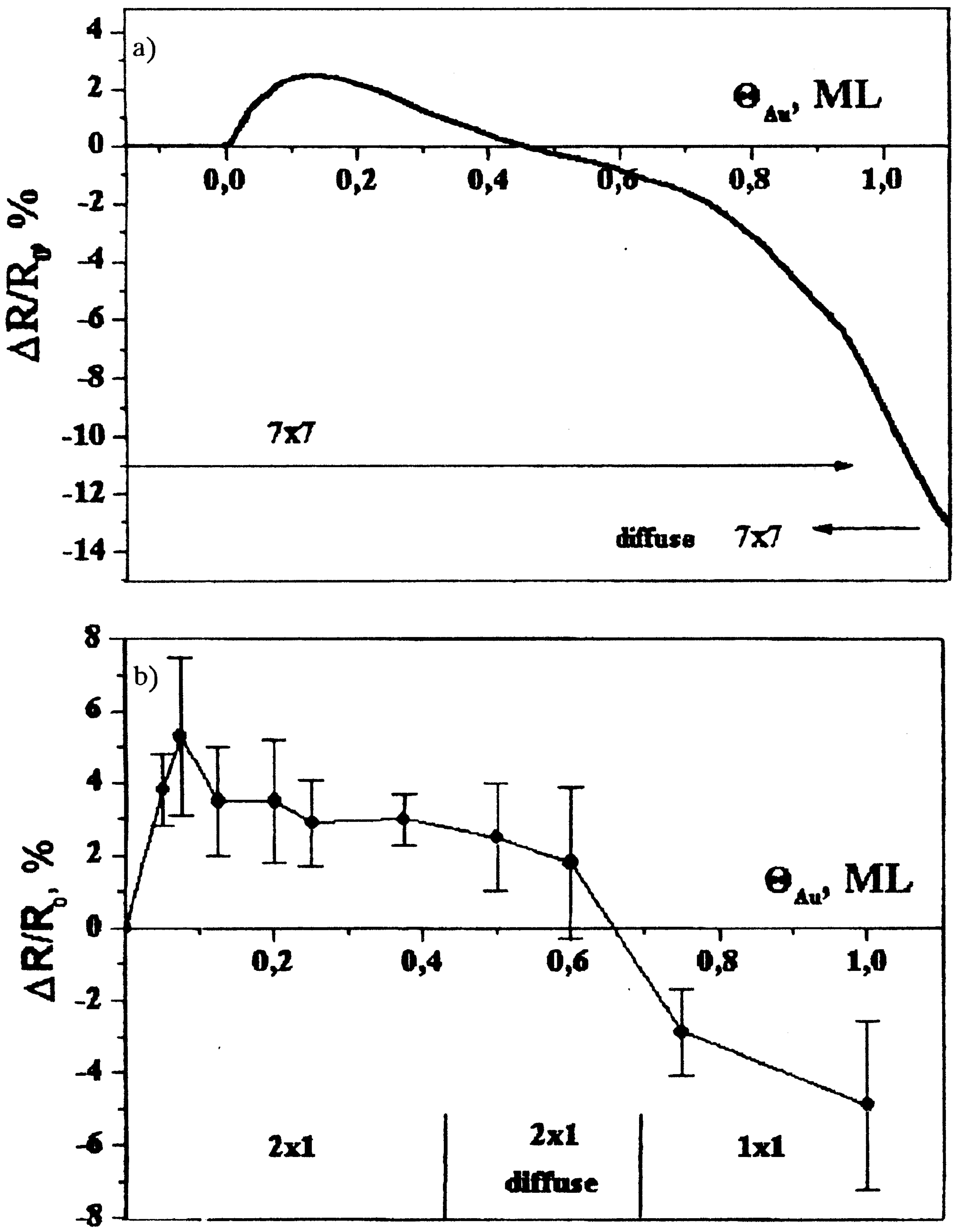

Figure 1. Changes in the surface resistivity during RT deposition of Au onto Si(111) (a) and Si(100) (b) surfaces.

resistivity is explained by conduction through the conductive islands grown on the surface.

The surface conductivity was measured for Si(100)$\sqrt{26}\times 3$-Au and Si(111)5×2-Au surface phases. It should be pointed out that during the gold deposition on heated silicon the substrate surface resistivity measured after cooling down the silicon substrate to room temperature is decreased [12]. In other words, the surface conductivity of substrates with the gold surface phase is increased. In this case the ordered Si-Au surface phases on silicon are formed leading to the formation of the additional conductivity channel that increases the conductance.

Surface phase	Θ_{Au}, ML	$\Delta\sigma =$ $\sigma_s(sp) - \sigma_s(a.c.\ Si\ surface)$, $\times 10^{-5} Ohm^{-1} \cdot square$
$Si(111)5 \times 2 - Au$	0.4	5.0 ± 1.0
$Si(100)c(8 \times 2) - Au$	0.5	6.0 ± 1.9
$Si(100)\sqrt{26} \times 3 - Au$	1.0	11.1 ± 0.8

Table 1. The surface conductivity of the silicon samples with Si-Au surface phases.

The values of conductivity calculated from experimental data are shown in Table 1. Notice that the surface conductivity for the Au/Si system is distinctly higher than that for the clean Si (for both Si(100)2 × 1 and Si(111)7 × 7 surface phases). We propose that the conductance of the surface phase is determined by the conductance through the state density of the surface phase if above mentioned reasons (surface space-charge layer, surface roughness, conductive islands grown on the surface, metastable two-dimensional gas phase) do not influence the surface transport properties. The obtained results were qualitatively confirmed for both n–type and p–type silicon samples.

4. Conclusion

The surface conductivity for the Au/Si(111) and Au/Si(100) systems was measured. Initially, at gold deposition onto Si samples the surface conductivity at room temperature is decreased due to the destruction of the Si surface phase. Further, the surface conductivity is increased because of the formation of the metal gold islands on the surface. The surface conductivity of the samples with the Si-Au surface phases was determined to be higher than that for Si samples with Si(100)2 × 1 and Si(111)7 × 7 surface phases.

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