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THE OPTICAL AND THE ELECTRONIC RESPONSE OF THE Ge(1 1 1)–$c(2 \times 8)$ SURFACE TO O_2 EXPOSURE

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This Communication describes a study concerning the interaction of molecular oxygen with a clean Ge(1 1 1)–$c(2 \times 8)$ surface. This reaction has been studied by *in situ* monitoring the ellipsometric reflection and the surface conductance. In order to explain the experimental results a model is proposed assuming a gradual disappearance of donor and acceptor surface states. The final stage in the adsorption process is characterized by the saturation of an acceptor surface state related to an optical transition at $h\nu = 1.9\,\text{eV}$.

SURFACE states can be characterized by various methods: photoemission, scanning tunneling microscopy, field emission, electrical measurements, ion-neutralization spectroscopy and ellipsometry. Frequently oxygen adsorption is used to generate a bulk-like electronic structure in the surface region. The difference between the clean and the adsorbed state serves to identify the electronic structure of the clean surface [1–3]. This procedure is also employed in the present paper. During oxygen adsorption both the surface conductance and the ellipsometric parameters are continuously followed. Small variations in the density of surface states (independent of their distance to the Fermi level) can be detected accurately with surface conductance measurements. By means of differential ellipsometry, the excitation of electrons from filled to empty surface states is studied and information is gathered containing joint properties of both types of bands. A relation between ellipsometric quantities and surface conductance is to be expected. For the interpretation of the results of our optical and electrical measurements we use a simple model which gives a relation between the ellipsometric parameter ψ and the surface conductance σ_s.

The experiments were performed in a stainless steel UHV system equipped with a single-pass cylindrical mirror analyzer for Auger electron spectroscopy, a spectroscopic RAE ellipsometer and an arrangement for surface conductance measurements [9]. The base pressure obtained was $1 \cdot 10^{-10}$ torr. The cleaning procedure for obtaining a clean Ge(1 1 1)–$c(2 \times 8)$ surface consisted of several cycles of Ar^+ bombardment ($\alpha = 45°$, 800 eV, $2\,\mu\text{A cm}^{-2}$) and annealing at 850 K [12–17]. Following this procedure, the intensity of the carbon peak was below the detection limit of the Auger spectrometer.

At equilibrium the surface charge density Q_{ss} is compensated by the space charge density Q_{sc}:

$$Q_{sc} = -Q_{ss} = [\Sigma e N_{sa} f_{sa} - \Sigma e N_{sd}(1 - f_{sd})], \quad (1)$$

where N_{sa} is the density of acceptor surface states with energy E_a and Fermi factor f_{sa}. In an analogous way N_{sd} is the density of donor surface states with energy E_d and Fermi factor f_{sd}. The bombarded-annealed germanium (1 1 1) surface is strongly p type [4–9]. For this case the surface conductance σ_s is given by

$$\sigma_s \simeq e\mu_{ps}[\Sigma N_{sa}^* - \Sigma N_{sd}^*], \quad (2)$$

where

$$N_{sa}^* = N_{sa} f_{sa} \quad \text{and} \quad N_{sd}^* = N_{sd}(1 - f_{sd}),$$

in which μ_{ps} is the mobility of the holes in the space charge layer. It is usually assumed that μ_{ps} is slightly smaller than the corresponding bulk value [10]. For $d\sigma_s$ one has in differential form

$$d\sigma_s \simeq e\mu_{ps}[\Sigma\, dN_{sa}^* - \Sigma\, dN_{sd}^*]. \quad (3)$$

In ellipsometry two parameters are measured, the relative phase difference (Δ) and the relative amplitude ratio (related to ψ) of the two components of the polarized light wave, parallel and perpendicular to the plane of incidence, upon reflection from a surface. The changes in these parameters upon oxygen adsorption were recorded as a function of the photon energy [9]. We have found optical transitions at 1.9, 2.3 and 3 eV after the growth of one monolayer of oxygen. The surface conductance was maximal at an oxygen coverage of 0.15 monolayer were we found transitions

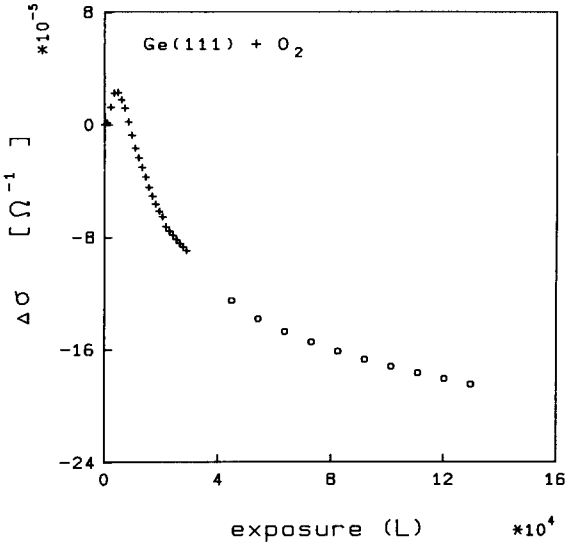

Fig. 1. Variation of the surface conductivity upon oxygen exposure. (+ $p = 5 \cdot 10^{-6}$ torr, o $p = 4 \cdot 10^{-5}$ torr).

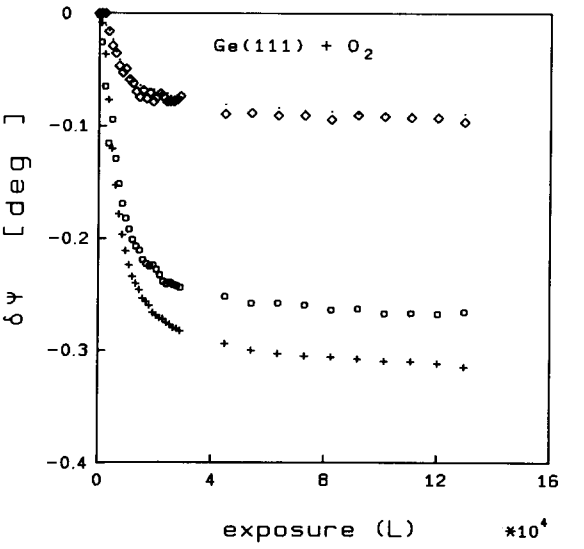

Fig. 2. Variation of the ellipsometric parameter ψ at optically active transitions upon oxygen exposure. (+ $h\nu = 1.9$ eV, o $h\nu = 1.7$ eV, · $h\nu = 2.3$ eV, ◇ $h\nu = 3$ eV).

at 1.7, 2.3 and 3 eV [9]. In order to obtain some insight we show the change in ψ during oxygen adsorption retaining only first order terms in d_{ss}. This is essentially the Drude approximation [11] resulting into:

$$\Delta\psi_{ss} \sim (h\nu/n_b^2)[\mathrm{Im}\,(\varepsilon_{ss} - \varepsilon_b)]d_{ss}, \tag{4}$$

where ε_{ss} is the dielectric constant of the surface states and $\varepsilon_b = (n_b - ik_b)^2$ that of the bulk [9], d_{ss} is the thickness of the surface states layer. The effect of the thin oxide layer on the surface is neglected [9]. The relevant parameter for the transition probability between occupied and unoccupied electron states is $(h\nu)^2\,\mathrm{Im}\,(\varepsilon_b)$ [18]. If we assume an occupied state with density N_{sa}^* and energy E_a and an unoccupied state with density N_{sd}^* and energy E_d the joint density-of-states is given by $N_{sa}^* N_{sd}^*$. Therefore:

$$\Delta\psi_{ss} = \Sigma\,\Delta\psi_{ss,i} \sim \Sigma\, N_{sa}^* N_{sd}^*/(h\nu\, n_b^2), \tag{5}$$

(summation over the optical transitions $h\nu_i = 1.7, 1.9, 2.3, 3$ eV).

In differential form

$$\Sigma\,\mathrm{d}\psi_{ss}(h\nu\, n_b^2) \sim \Sigma[\mathrm{d}N_{sa}^* N_{sd}^* + \mathrm{d}N_{sd}^* N_{sa}^*]. \tag{6}$$

If at room temperature molecular oxygen is added the p type surface conductivity first increased and then decreased (see Fig. 1). As mentioned before maximum surface conductance occurs at an oxygen coverage of 0.15 monolayer. Under the same conditions Surnev [12] found from work function measurements a change in the elementary dipole moment.

During oxygen adsorption $\delta\psi$ is followed continuously on the peaks at 1.7, 1.9, 2.3 and 3 eV (Fig. 2). A graph of $\mathrm{d}\sigma_s$ vs $\Sigma\,\mathrm{d}\psi(h\nu\, n_b^2)$ shows an initial and a final linear behaviour separated by a transition around 0.15 monolayer equivalent (Fig. 3). We can understand the two straight lines assuming the following conditions, see formulas (3) and (6):

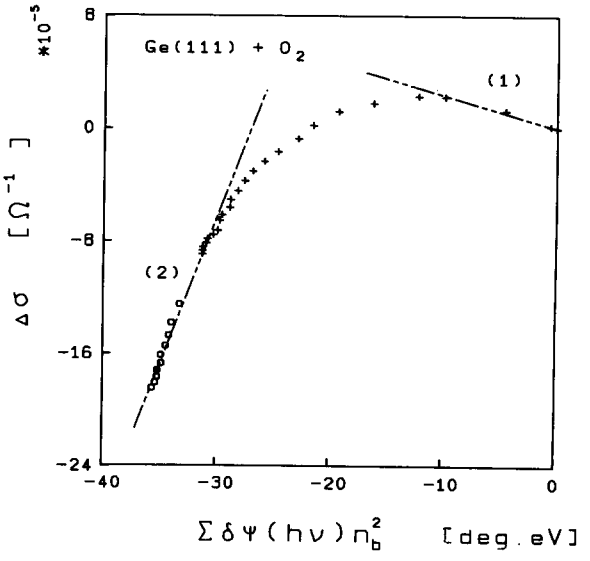

Fig. 3. Variation of the surface conductivity versus $\Sigma\,\delta\psi(h\nu n_b^2)$. (+ $p = 5 \cdot 10^{-6}$ torr, o $p = 4 \cdot 10^{-5}$ torr).

First stage: assume $\mathrm{d}N_{sa}^* = 0$ (N_{sa}^* = constant) and one of the $\mathrm{d}N_{sd}^*$ terms is dominating. In this case the slope in Fig. 3 is proportionally to $-e\mu_{ps}/N_{sa}^*$ (N_{sa}^* of dominating transition). The relation is weak, however the slope is negative and almost constant indicating that mainly donor surface states are disappearing.

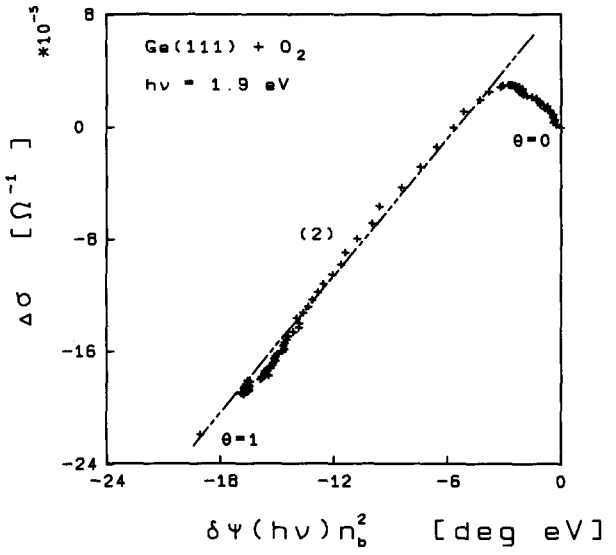

Fig. 4. Variation of the surface conductivity versus $\delta\psi(h\nu n_b^2)$ at $h\nu = 1.9\,\text{eV}$. Data taken from [9].

Second stage: assume $dN_{sd}^* = 0$ (N_{sd}^* = constant) and one of the dN_{sa}^* terms is dominating. In this case the slope in Fig. 3 is proportionally to $e\mu_{ps}/N_{sd}^*$ (N_{sd}^* of dominating transition). It is likely that the transition at 1.9 eV is related to the dominating acceptor surface state (see Fig. 4).

Summarizing we have described the adsorption process by a two-stage saturation of surface states, first mainly the donor states and secondly the acceptor states.

The relation between $d\sigma_s$ and $\delta\psi$ at $h\nu = 1.9\,\text{eV}$ shows that the second stage is dominated by the removal of one acceptor surface state only.

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