Adsorption of atomic oxygen (N_2O) on a clean Ge(001) surface

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We present the results of a study concerning the interaction of atomic oxygen (as released by decomposition of N_2O) with the clean Ge(001) 2×1 surface at 300 K. Ellipsometry in the photon energy range of 1.5–4 eV, surface conductance measurements and Auger electron spectroscopy (AES) have been used to monitor this solid–gas reaction. Adsorption of N_2O on the clean Ge(001) surface was found to terminate at monolayer coverage. As compared to the adsorption of molecular oxygen (O_2), we observed in the joint density of states a splitting of the 1.8 eV peak into peaks at 1.7 and 2 eV plus an additional weak shoulder at 2.3 eV. Surface conductance measurements indicate that the adsorption process is dominated by the removal of filled surface states (dimer and dangling bond of the up atom). Atomic oxygen goes into a bridging position between top layer Ge atoms, in the initial stage first by decomposing at the Ge–Ge dimer bonds. The adsorption behavior of N_2O at the Ge(001) 2×1 surface is similar to that at the closely related Si(001) 2×1 surface [Keim *et al.*, Surf. Sci. **180**, 565 (1987)]. Our results confirm the site specificity of the N_2O molecule.

I. INTRODUCTION

Although substantial research has been devoted to the Ge(001) surface, numerous uncertainties remain concerning the structure of the bare surface and that of the oxide interface with this surface. The renewed interest in Ge surfaces is mainly caused by the recent progress in the strained-layer systems such as the Ge_xSi_{1-x}/Si heterojunction. The unreconstructed Ge(001) surface consists of divalent Ge atoms, each bonded to two subsurface germanium atoms. This surface is generally thought to reconstruct to form a nominal (2×1) surface unit cell by asymmetric dimerization of nearest-neighbor (nn) surface atoms. However, higher-order reconstructions [$c(4 \times 2)$ and $p(2 \times 2)$],¹ generated by various ordered arrangements of asymmetric dimers, have been observed on the Ge(001) surface.

The interaction of oxygen with Ge and Si surfaces has been the subject of many studies. In spite of this enormous effort there is still some controversy about the initial binding state of oxygen. For Si surfaces it is now generally accepted that oxygen adsorbs dissociatively mainly forming Si–O–Si bridge configurations.² For the initial step of adsorption on Si(111) 7×7 , however, it has been shown that a metastable intermediate state is involved which is likely to be a molecular precursor to the stable dissociated state.^{2,3} An STM study of the oxidation of this surface reveals that defect sites with the appearance of missing adatoms act as nucleation sites for the oxidation process.⁴

Upon surveying the literature (see, e.g., Refs. 5–9) it appears that further chemisorption studies using only molecular oxygen (O_2) shall not provide significant improvement in the understanding of the atomic and electronic nature of the oxygen covered germanium surface. We therefore felt that the application of atomic oxygen (as released by N_2O) in the study on the mechanisms of the initial stages of oxidation on Ge(001) would be helpful. This approach has been successfully applied to the Si(001) 2×1 surface by Keim, Wolterbeek, and van Silfhout.¹⁰ They found that decomposition of N_2O mainly occurs at those surface Si atoms which

have a dimer and a dangling bond. According to their model each oxygen atom lies essentially in the surface plane in a bridge bonded position leading to a well defined saturated monatomic oxygen layer, in the case of an ideal defect-free Si(001) 2×1 surface. Additional proof in favor of their model for the uptake of atomic oxygen (O) on an ideal clean Si(001) 2×1 surface as experimentally predicted in Ref. 10 has been given, very recently, from semiempirical chemical cluster calculations¹¹ and from theoretical work on the adsorption of atomic oxygen at the 2×1 reconstructed Si(001) surface.¹²

With differential ellipsometry and surface conductance measurements information of the electronic structure of the germanium can be obtained.^{13–15} Two of the advantages of using these techniques are their essentially nonperturbing nature and the possibility to follow *in situ* the adsorption process. With Auger electron spectroscopy (AES) a quantitative analysis can be made of the different types of atoms in the surface region.

II. EXPERIMENTAL

All experiments were performed in a stainless steel UHV system described previously,¹³ with additional facilities for AES, ion bombardment and evacuation of the reaction chamber by a 200 ℓ/s turbomolecular pump (Pfeiffer TSU 200). The base pressure of the UHV system was $\sim 1 \times 10^{-10}$ Torr. Upon reaching this static condition the reaction chamber was then evacuated by a 400 ℓ/s Riber ion pump with titanium sublimator. Vacuum cleanliness was checked by a Riber QMM 16 quadrupole mass spectrometer. The germanium sample was mounted onto a sample holder of a homemade manipulator which allowed rotation and translation (in the X, Y, and Z direction) of the sample.

The germanium sample ($10 \times 30 \times 0.3 \text{ mm}^3$) was made out of a 20 $\Omega \text{ cm}$, *n*-type crystal in the (001) orientation. Prior to mounting the crystal was ultrasonically cleaned in ethanol.¹⁰ A clean surface was obtained by cycles of sputter-

ing (800 eV Ar ions, $2 \mu\text{A cm}^{-2}$, 20 min, angle of incidence 45°) and annealing (850 K, 40 min).^{14,16,17} During sputtering the crystal was also heated to 700 K for ~ 10 min, followed by slow cooling.

Spectroscopic ellipsometry measurements were performed with a rotating analyzer in the photon energy range (E) of 1.5–4 eV. The ellipsometric parameters Δ and ψ ($\rho = \tan \psi e^{i\Delta}$) were determined by the two-zone method. We have used tetrasil windows which are transparent for wavelengths in the region of 150 nm to $3 \mu\text{m}$. The experimental errors in $\delta\Delta$ and $\delta\psi$ are $< 0.01^\circ$, corresponding to an error in the magnitude of the $\text{Im}(\epsilon_{ss} - \epsilon_b)$ curve of < 1 . The symbols ϵ_b and ϵ_{ss} stand for the dielectric constants of the bulk and the surface states layer, respectively. For the surface conductance measurements four titanium contacts were evaporated on the sample through a tantalum mask.¹⁷ A chopped constant current was sent through the outer pair of contacts of the sample, while the resulting potential was measured between the inner pair of contacts. In this way nonlinear behavior of the metal–semiconductor contact is eliminated. Use of alternating current averages out any thermo or photovoltage effect resulting from a nonuniform sample temperature or illumination. The Auger spectra were recorded using a primary beam energy of 2 keV, primary current density of $\sim 0.5 \mu\text{A cm}^{-2}$, modulation voltage of the energy analyzer 3 V_{pp}, a sweep rate of 1 eV/s and a lock-in time constant of ≤ 1 s.

III. RESULTS AND DISCUSSION

No nitrogen was detected in the Auger spectra, confirming that the overall reaction is $\text{N}_2\text{O} \rightarrow \text{N}_2' + \text{O}_{ad}$. The adsorption of N₂O terminates at monolayer (ML) coverage [the peak-to-peak height of oxygen (510 eV) divided by the peak-to-peak height of germanium (1147 eV) saturates at 0.7, which corresponds to (~ 1 ML¹⁸)]. Since the sticking coefficient of N₂O on Ge(001) is extremely low ($< 10^{-7}$) the adsorption experiments were performed at relatively high pressures ranging from 10^{-2} to 1 Torr. A well defined dose of N₂O gas was leaked via a valve into the reaction chamber. During gas exposure we did not pump at the reaction chamber. The volume of the reaction chamber is known so the pressure could be calculated.

In Figs. 1 and 2 are shown the differences in the ellipsometric parameters $\delta\psi$ and $\delta\Delta$, before and after exposing a clean Ge(001) surface to N₂O at saturation. The $\delta\psi$ and $\delta\Delta$ versus E curves display well observable structure. This structure was interpreted as due to a substrate change upon chemical adsorption, i.e., the saturation of the dangling bonds which exist at the clean surface. Chemisorption on clean germanium surfaces might cause a change in the (bulk) optical constants due to the Franz–Keldysh effect.¹⁹ Nannarone *et al.*²⁰ mentioned that the change in reflectivity brought about by the oxide layer can in principle not be neglected. These authors argue that such a term is very small except near critical points of the bulk structure and in germanium it is negligible below 3.5 eV.²⁰

The clean germanium surface is considered to consist of a bulk substrate (ϵ_b) covered with a surface states layer with optical constants (ϵ_{ss}) different from the bulk (it can be

FIG. 1. $\delta\psi = \psi(\text{N}_2\text{O})_{1\text{ ML}} - \psi(\text{clean})$ as a function of photon energy (E).

shown that the choice of the layer thickness has no influence on the interpretation²¹). The relevant parameter for the transitions involving surface states is the difference between the imaginary part of the dielectric function of the surface states layer and that of the bulk at corresponding photon energies, i.e., $\text{Im}(\epsilon_{ss} - \epsilon_b)$. The $\text{Im}(\epsilon_{ss} - \epsilon_b)$ curve for the Ge(001) surface as a function of $h\nu$ is given in Fig. 3. In the photon energy range of 1.5–4 eV the influence of a ML of oxygen on the value of $\text{Im}(\epsilon_{ss} - \epsilon_b)$ can be calculated^{13,14} but its influence on the structure of the curve is negligible. We observed in the joint density of states, as compared to the adsorption of molecular oxygen,¹⁴ a splitting of the 1.8 eV peak into peaks at 1.7 and 2 eV plus an additional weak

FIG. 2. $\delta\Delta = \Delta(\text{N}_2\text{O})_{1\text{ ML}} - \Delta(\text{clean})$ as a function of photon energy (E).

FIG. 3. The imaginary part of the difference in complex dielectric constant $\text{Im}(\epsilon_{ss} - \epsilon_b)$ between the surface states layer and the bulk substrate for the clean Ge(001) surface as a function of the photon energy (E).

shoulder at 2.3 eV. The optical transition at 3.3 eV as observed with O₂ adsorption is now divided into two contributions at ~ 3 and 3.5 eV, respectively. The existence of higher order reconstructions like $c(4 \times 2)$ and $p(2 \times 2)$ ¹ together with the site specific adsorption behavior of the N₂O molecule¹⁰ may account for the observed splitting of the peaks in the optical spectra. A similar phenomenon is observed at the Si(001)2 $\times$ 1 surface.¹⁰ During N₂O exposure the ellipsometric changes at the optical transitions at 1.9 and 3.2 eV have been recorded (1.9 and 3.2 eV are approximately the main peaks in Figs. 1 and 3). The results are depicted in Fig. 4. By referring to theoretical results²² and comparison with the closely related Si(001)2 $\times$ 1 surface we suggest that the

FIG. 4. Conductance change $\Delta\sigma$, and variation of the ellipsometric parameter ψ at the optical transition at 1.9 and 3.2 eV vs N₂O exposure. The asterisk indicates the stage at which the pressure increases from 0.05 to 0.5 Torr.

optical transition at 1.9 eV can be attributed to a transition from the filled dangling bond of the up atom to the empty dangling bond of the down atom.^{1,10,22} We also suggest^{1,10,22} that at least the filled dimer surface state is involved in the optical transition at 3.2 eV (filled dimer to empty dimer, or filled dimer to empty dangling bond of the down atom). The change in $\psi(h\nu)$ during gas adsorption is in first order proportional to $d_{ss} \text{Im}(\epsilon_{ss} - \epsilon_b)$, which is essentially the Drude approximation¹⁵

$$\delta\psi(h\nu) \sim [h\nu/n_b^2] [\text{Im}(\epsilon_{ss} - \epsilon_b)] d_{ss} = J(h\nu)/[n_b^2 h\nu], \quad (1)$$

where $\epsilon_b = (n_b - ik_b)^2$, d_{ss} is the thickness of the surface states layer, and $h\nu$ is the photon energy. The joint density of surface states,¹⁵ $J(h\nu)$, is proportional to $(h\nu)^2 \text{Im}(\epsilon_{ss} - \epsilon_b)$. From Fig. 4 it can be seen that the initial stage of the chemisorption of atomic oxygen via decomposition of N₂O mainly leads to a removal of dimer bond surface states (3.2 eV). The removal of the filled dangling bond surface state, however, is slow (1.9 eV). Its rate of removal increases during increasing exposure. Atomic oxygen is strongly electronegative (1.45 eV) so it is very likely that acceptor surface states (filled surface states) have appreciable reactivity towards the oxygen atom. Calculations performed by Yin and Cohen²³ indicate that the electronic charge density at the dimer is higher than at the dangling bond up. Simple geometrical considerations may also explain why the oxygen atom prefers to go into a bridging position between the two Ge atoms which constitute the dimer. For simplification we consider the growth of the oxide layer to occur in the $[1\bar{1}0]$ direction only (the axis between the two atoms of the dimer is along the $[1\bar{1}0]$ direction). Smaller distances (and possibly less strain) is therefore involved in the formation of a Ge-O-Ge group at the dimer than between two Ge atoms of nn dimers. Due to the formation of Ge-O-Ge groups at two nn dimers, the distance between the up atom of one dimer and the adjacent down atom of the nn dimer becomes smaller. Consequently the incoming oxygen atom may attack this site (1.9 eV transition) as well as the dimer (3.2 eV transition). A similar behavior is observed for the reaction of N₂O with the Si(001)2 $\times$ 1 surface.¹⁰

If at room temperature N₂O was added the p -type surface conductance first decreased, then increased and finally decreased again (see Fig. 4). By definition the surface conductance σ_s is given by

$$\sigma_s = e(\mu_{ns}\Delta N + \mu_{ps}\Delta P), \quad (2)$$

where e is the elementary charge, μ_{ns} and μ_{ps} are effective carrier mobilities at the surface and ΔN , ΔP the excess electron and hole concentrations per unit surface area. The surface mobilities are replaced by their corresponding bulk values, this assumption introduces errors of $\sim 20\%$, see, for example, Refs. 24 and 25. The changes in surface conductance are attributed to changes in the surface space charge layer, i.e., in the density of surface states. Since the condition of electrical neutrality must be satisfied we have

$$\sum_i -eN_{sai}f_{sai} + \sum_j eN_{sdj}(1 - f_{sdj}) = e[\Delta N - \Delta P], \quad (3)$$

where N_{sa} is the density of filled surface states with Fermi

factor f_{sa} , and N_{sd} is the density of empty surface states with Fermi factor f_{sd} . Taking Eqs. (2) and (3) and Fig. 4 into account it can be concluded that adsorption of atomic oxygen on the Ge(001) 2×1 surface is dominated by the removal of filled surface states, i.e., the filled dimer and the filled dangling bond up surface states. The small increase in surface conductance must be due to the quenching of empty surface states, for example the dangling bond of the down atom or the antibonding dimer.

IV. CONCLUDING REMARKS

The most important conclusion of this paper is that an atomically clean Ge(001) 2×1 surface can be oxidized in a very controlled way by using nitrous oxide at 300 K. Decomposition of N₂O on the Ge(001) surface was found to terminate at ML coverage, this behavior is in accordance with the corresponding Si(001) surface. We have found evidence that first the dimers are attacked by atomic oxygen, followed by quenching of the filled dangling bonds. In agreement with STM measurements we found evidence in our ellipsometric measurements for the existence of higher order reconstructions like $c(4 \times 2)$ and $p(2 \times 2)$, on the Ge(001) 2×1 surface at room temperature.

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