PHYSICAL REVIEW B VOLUME 42, NUMBER 10 1 OCTOBER 1990

Monitoring low-coverage surface chemistry with bulk transport: NO_2 dissociation and oxygen penetration at a GaAs(110) surface

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(Received 6 June 1990)

We report an example of the effects of surface chemistry on bulk electronic properties. We study the dissociative adsorption of NO_2 on a high-resistance GaAs(110) crystal surface. We show that the dissociation can be accurately followed with high sensitivity by monitoring the sample conductance. We use infrared spectroscopy, He specular scattering, and Auger spectroscopy, to specify the chemical processes involved. In addition to the dissociative adsorption, both the conductance and the minority-carrier lifetime show that a second subsequent rate process occurs, which we identify as penetration of chemisorbed oxygen into the bulk.

We demonstrate that low-coverage chemical processes at surfaces can be followed with high sensitivity by monitoring their effect on bulk average conductance in low-carrier-density semiconductors. The example we have studied is the dissociative adsorption of NO_2 on defect-compensated GaAs(110). We are able to follow the deposition of oxygen atoms by the change in sample conductance. In addition, the conductance clearly indicates a second process occurring subsequent to the oxygen deposition. This process would not have been observed with standard surface chemistry techniques. By combining the conductance measurements with specular He beam scattering, Fourier transform infrared spectroscopy, and carrier lifetime measurements, we identify the chemical processes associated with the conductance changes. Specifically, we determine the probability of low-coverage NO_2 dissociative adsorption which produces an oxidized surface. Further, we show that a small fraction of the resulting adsorbed oxygen penetrates into the bulk to form a deep electronic level which further affects the material transport properties. This work is an example of how transport measurements, in moderate to high-resistance materials, can play an informative role in sorting out the complexities that are often a part of the mechanisms of surface chemistry.

The change in conductance upon chemical adsorption has long been the subject of research in the area of chemical sensors.[1] In general, that research has been associated with very-high-band-gap materials (oxides) in order to reduce the number of free charge carriers compared to surface sites. In this work we demonstrate that for the additional class of materials of compensated semiconductors, the sensitivity and temporal response of the measured transport are sufficient to provide valuable indications of complex low-coverage chemical change. Specifically, when combined with sensitive contemporary surface-science techniques, subtle chemical processes can be revealed which often undermine the simple exploitation of these effects. More detailed descriptions of these experiments and analysis will be published elsewhere.[2]

These experiments were performed on defect-compensated ($EL2$) GaAs(110) ($\rho = 2\times10^6$ Ωcm) crystals.[3,4] Two different experimental setups were employed, which have been described in detail elsewhere.[5,6] The first apparatus combines capabilities for molecular-beam scattering with measurements of average sample conductivity and carrier lifetimes.[5] It includes a molecular-beam source, Auger electron spectrometer (AES), low-energy electron diffraction optics (LEED), rotatable quadrupole mass spectrometer (QMS), and laser excitation (HeCd or HeNe) source and optics for carrier-lifetime measurements. The second apparatus[6] incorporates Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS), with AES, residual-gas mass spectrometry, and a background dosing capability.

The samples used in the spectroscopy apparatus and the molecular-beam apparatus were cut from the same crystal and polished together. The cleaning and annealing procedures were kept as similar as possible. The spectroscopic samples were beveled at 45° at each end so that the entering radiation underwent approximately 100 internal reflections before exciting.

A good example of the principal observation, which illustrates the effects of interest, is shown in Fig. 1. There we plot the simultaneous evolution of the substrate conductance and the attenuation of the scattered specular He beam, for a GaAs(110) sample at room temperature, during and subsequent to a low-pressure exposure (2×10^{-8} Torr) of NO_2. The incident angle of the He beam is 60° and the energy is 63 meV. The change in both signals is due to the slow buildup of adsorbed oxygen. Both NO_2 and the dissociation product NO rapidly desorb from the surface at room temperature so that their steady-state coverage is negligible. Note that both measurements are extremely sensitive to the changing chemical state of the sample surface. The exposure ceases after an adsorbate coverage of only $\sim$9% of a monolayer was obtained (calibrated by using an oxygen atom source). Upon cessation of the exposure, the specular He scattering signal, which decreased nearly linearly with time, stays quite constant indicating little further chemical or topographical change in the surface occurs. In contrast, the crystal conductance continues to substantially evolve for several minutes after the cessation of NO_2 exposure, and in the opposite direction to that corresponding to its initial change.[7]

The attenuation of the He specular beam has proven to

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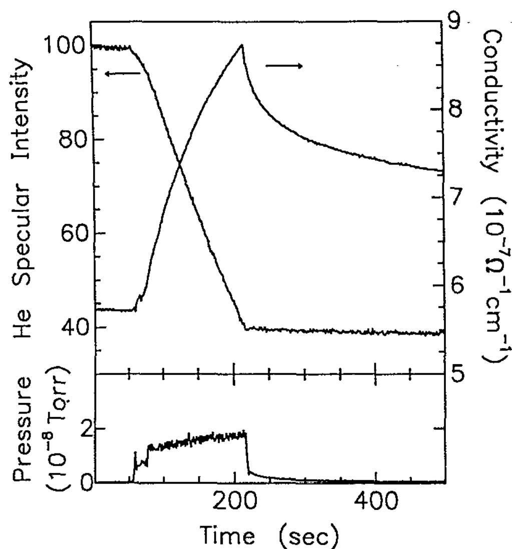

FIG. 1. Variation of the specular He intensity (left-hand-side ordinate) and crystal conductance (right-hand-side ordinate) with time. The period of NO_2 exposure ($P \sim 2\times10^{-8}$ Torr) is indicated. The result of the exposure is a $\sim$9% coverage of oxygen atoms. Note the flatness of the specular He intensity upon cessation of exposure, in contrast to the reversal of the change in conductance.

be straightforward to interpret in terms of the adsorbate total cross section for scattering out of the specular beam.[8] In these previous studies smooth substrate surfaces have been employed, that is surfaces for which the dominant elastic-scattering channel is the specular beam. For these examples, it can be shown[9] that the adsorbate cross sections are close to total-scattering cross sections observed in the gas phase, i.e., $> 10^2$ Å^2. For a surface with a strongly corrugated He scattering potential, such as GaAs(110),[10] we have observed a variation in sensitivity to adsorbates for this scattering process, depending on incident conditions and the diffraction beam used to follow the adsorption, presumably due to the strong coupling between diffraction channels. However, for these experiments we chose incident conditions for which the oxygen adsorbate had a strong effect on the He specular beam intensity, corresponding to an effective cross section of $\sim$240 Å^2, giving a sensitivity to adsorbate coverage of $\sim \pm 2\times10^{-3}$ monolayers.[11] Thus, in Fig. 1, the continual decrease in the He specular beam intensity with NO_2 exposure corresponds to an average dissociative adsorption probability of $\sim$0.03 (dependent on surface-defect density[2(b)]) with a final coverage of 8.6%. (For comparison, the apparent dissociative adsorption probability of O_2 ranges from $\sim 10^{-7}$–10^{-9} depending on the surface quality and/or oxygen purity). The subsequent constant signal is a clear indication that upon cessation of exposure, little further change in the surface adatom population occurs (to within $\pm$0.2%).

Similarly, upon exposure to NO_2, the bulk average conductance of the GaAs sample begins to increase (Fig. 1). We interpret this as due to the change in the surface potential upon dissociative adsorption of NO_2, which results in the deposition of the electronegative oxygen atom (and rapid desorption of the product NO) at room temperature. The GaAs sample has a resistivity nearly that of intrinsic material and is slightly *p* conducting. O deposition changes the surface potential negatively with respect to the bulk, that is the bands bend up at the surface, or electron density is removed from the surface region.[12] Thus the population of holes increases and consequently the conductance increases upon O adsorption. For the initial resistance of 5×10^7 Ω, the initial rate of change corresponds to 4×10^8 Ω per monolayer, indicating a sensitivity to coverage at least comparable to that from the attenuation of He specular scattering. In contrast to the attenuation of the He specular scattering, the conductance *continues to change* after cessation of the NO_2 exposure, but in the opposite direction to that associated with the change in the surface potential due to oxygen deposition. We conclude from Fig. 1 that a second rate process occurs upon oxidation of GaAs(110), which continues after cessation of NO_2 exposure. It appears to affect only the (small) free-carrier density in the bulk as it produces no measurable effect at the surface at the $\pm$0.2% monolayer level.

In Fig. 2 we plot the minority carrier lifetime versus time. The time axis includes a period of NO_2 exposure and a subsequent period where the relaxation in the conductance was observed (Fig. 1) after cessation of exposure. For comparison the evolution of the sample conductance is included. The minority carrier lifetimes were measured as described in Ref. 13. Briefly, a HeNe laser (λ=532 nm) illuminated the sample for a period long enough for the resulting increased conductance to reach steady state (> 1 msec). An effective minority carrier lifetime was extracted from the steady-state increased carrier concentration under illumination and the measured absorbed power (creation rate). The derived lifetime was plotted as a function of laser power over several orders of magnitude until at low power the Shockley-Read-Hall[12] regime (τ independent of power) was reached. We used this lifetime as an indicator of a change

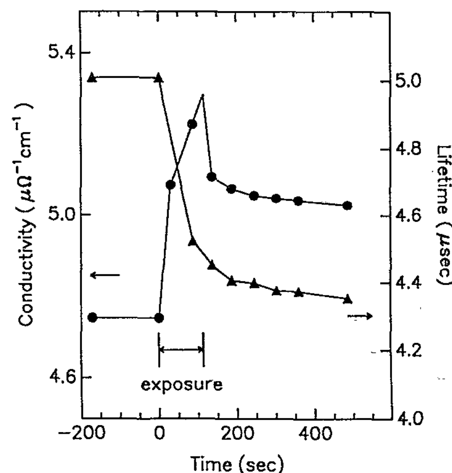

FIG. 2. Comparison of the minority carrier lifetime and crystal conductance with time, which includes a period of exposure to NO_2 ($P = 2\times10^{-8}$ Torr). Both measurements continue to evolve with time upon cessation of exposure.

in the material properties.

The continual change in carrier lifetime during and subsequent to the adsorption of oxygen atoms, when considered with the constancy of the specular He beam, and the conductance behavior, leads directly to the conclusion that a slow chemical change is occurring in a subsurface region or even deeper in the bulk, as a consequence of oxygen chemisorption, and with which a change in the electronic levels in this region is associated.

In Fig. 3 we plot an FTIR-RAS spectrum obtained after NO_2 exposure at 100 K. We emphasize that the spectrum shown is a ratio of infrared transmission before and after exposure. One may note a strong absorption at 782 cm^{-1} and several weak features at 715 cm^{-1} and in the range 1200–1800 cm^{-1}. For the purpose of this paper we concentrate only on the features at 782 and 715 cm^{-1}. The higher-frequency features become more pronounced at higher exposures. A complete analysis of all the spectroscopic data will appear elsewhere.[2(a)] The strong mode at 782 cm^{-1} is assigned to chemisorbed atomic oxygen on the GaAs(110) terrace, which results from dissociated NO_2. Specifically, we attribute this mode to the oxygen-Ga stretching vibration.[2(a)] This assignment was confirmed by use of oxygen and nitrogen isotopes in NO_2. We note that at lower coverages the chemistry of NO_2 adsorbed on GaAs(110) is more complex. However, at low coverages we have shown[2(b)] the only significant surface process which occurs is the adsorption followed quickly (<1 msec) by reevaporation of most of the NO_2. In parallel, there is a small probability of NO_2 dissociation to deposit oxygen (782 cm^{-1}) which is followed by rapid NO desorption. The weak feature at 715 cm^{-1} has recently been reported elsewhere[14] and assigned to substitutional oxygen atoms bridge bonded to Ga in the *bulk* of GaAs. Since the spectrum in Fig. 3 is the ratio of spectra taken before and after NO_2 exposure, this bulk feature at 715 cm^{-1} arises due to the chemistry asociated with NO_2 at the surface. This is a direct indication that a small amount[15] of oxygen has penetrated the surface of GaAs(110) and reacted in the subsurface region or even deeper in the bulk. To obtain this spectrum required signal averaging for over 400 s. Therefore, we are not able to compare the temporal evolution of this feature with the data of Fig. 1.

We note that oxygen atoms in the bulk are known to have an electronic level $\sim$0.4 eV below the conduction band.[16] We interpret the variation in conductance after the cessation of NO_2 exposure in terms of this bulk oxygen donor level. We suggest that chemisorbed O enters the bulk from the surface and ionizes (O^+),[16] and that most of these additional electrons recombine with and neutralize the holes which are the majority current carriers. The remaining holes on the bulk oxygen are immobile as their density is too low to form a band allowing transport. The carrier lifetime, as shown in Fig. 2, is comparably affected by the ionized bulk oxygen atoms. We suggest that they provide an increased number of trapping and recombination centers for the excess charge resulting from illumination. Thus they reduce the lifetime independent of the consequences of band bending. We note that we cannot exclude a change in the surface potential which can also affect the carrier lifetime. However, the abrupt reversal of direction of the excess surface conductance, upon cessation of NO_2 exposure, would cause at least a discontinuity in that part of the carrier lifetime attributable to the change in surface chemistry. This is not observed and the lifetime continues to change after cessation of the surface oxidation. Thus, we conclude the dominant factor affecting the carrier lifetime is also a bulk process, which continues after the surface oxidation ceases.

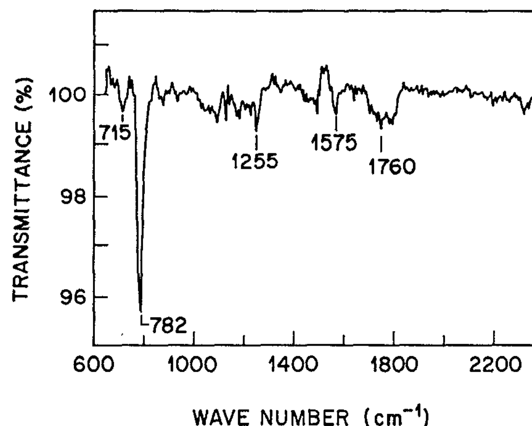

FIG. 3. Ratio of infrared transmission before and after exposure to 4.6 L of NO_2 ($1 L = 10^{-6}$ Torr s). The peak at 782 cm^{-1} corresponds to a surface oxygen vibration. The small feature at 715 cm^{-1} has been identified as oxygen in the bulk.

With the addition of molecular-beam-scattering results, reported elsewhere,[2(b)] we summarize what we think is the essence of the chemical action. NO_2 adsorbs molecularly with a high sticking probability ($> \frac{1}{2}$) on GaAs(110), and at room temperature most of the NO_2 desorbs quickly (residence time $< 10^{-3}$ s). A fraction of the adsorbed NO_2 finds a special site (defect) or configuration and dissociates, depositing an oxygen atom, and the product NO quickly desorbs. Most of the chemisorbed oxygen atoms remain on the (110) surface as indicated by the surface potential and the He specular reflectivity. A small fraction of the oxygen penetrates the surface (perhaps at defect sites), diffuses into the bulk (we are unable to make any predictions about the penetration depth), and produces an electronic donor level $\sim$0.4 eV below the conduction band. This additional chemical process was signaled by a change in transport properties and would not have been observed by standard surface-science techniques. Indeed, the confirmation of the oxygen penetration by FTIR-RAS was possible because it is also sensitive to the spectral features of the bulk which change upon a surface process.

K.K. acknowledges partial support from the Alexander von Humboldt Foundation.

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