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Role of O_2 negative-ion formation in low-energy electron-induced oxidation of InP(110)

Y. Chen, Y-S. Luo, J. M. Seo, and J. H. Weaver
Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

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We report surface oxidation induced by (1–8)-eV electrons incident on O_2 condensed on InP(110) at 30 K. The measured reaction cross sections are very much energy dependent with values of $(8\pm4)\times10^{-18}$, $(1\pm0.5)\times10^{-17}$, $(8\pm4)\times10^{-17}$, and $(2\pm1)\times10^{-16}$ cm^2 for electrons with energies of 1, 2, 5, and 8 eV, respectively. These cross sections exhibit the same energy dependence as molecular-oxygen negative-ion formation, and they are much larger than those related to dissociative electron attachment. The results show that resonant negative-ion formation of O_2^- is important in surface reactions induced by electron irradiation.

Studies of electron-stimulated oxidation of semiconductor surfaces have focused on high-energy electrons (from 50 eV to 300 keV) and their influence on room-temperature processes.[1-5] Surface-oxidation enhancement has been attributed to the dissociation of molecules of the oxidizing gas. Unfortunately, the high-energy electrons generate many secondary electrons with a broad energy distribution at lower kinetic energy, and it is impossible to relate the observed phenomena to any particular molecular channel. Furthermore, attempts to measure electron-stimulated reaction cross sections have been challenging at 300 K because molecular-adsorption kinetics must be involved. Recent reports of x-ray-induced oxidation of semiconductor surfaces have attributed reaction enhancement to the photogenerated secondary electrons.[6,7] Thus, experiments involving surface processes stimulated by low-energy electrons would be of interest in their own right and provide better understanding for photon-induced reactions as well.

In this paper, we report the study of InP(110) oxidation stimulated by electrons with kinetic energies of 1–8 eV for O_2 condensed on the surface at 30 K. We show that these electrons induce strong surface oxidation. Indeed, these results demonstrate that molecular-oxygen negative-ion resonant states play an important role in the initial stages of oxidation of InP(110) induced by low-energy electron irradiation. In particular, the energy dependencies and the magnitudes of the reaction cross sections are similar to those observed for molecular-oxygen negative-ion resonant-state formation. The dissociative electron-attachment process has too small a cross section to account for the reactions measured in our experiments.

The experiments were conducted in an ultrahigh-vacuum chamber equipped with a Mg x-ray source ($h\nu=1253.6$ eV) and a He discharge lamp for photoemission characterization of surface oxidation. Since photons are known to induce semiconductor surface oxidation,[6,7] care was taken to avoid x-ray irradiation when condensed O_2 was present. The He lamp was tuned to maximize He II emission ($h\nu=40.8$ eV), and the irradiation at this energy does not produce significant surface oxidation due to its weak intensity and the low number of secondary electrons generated. This is consistent with the report by Frankel *et al.*[8] that such low-intensity sources do not induce oxidation on GaAs(110) with physisorbed O_2. Even so, the irradiation time was minimized during data acquisition and, thus, the data shown here will appear a little noisy.

The electron source was the coaxial gun in a cylindrical mirror analyzer (CMA). Its primary energy was 13.5 eV, as determined by the elastic-peak position in the energy-distribution spectrum of the reflected beam. The energy spread was less than 0.5 eV, based on the width of the elastic peak. The sample was electrically biased so that the current through it could be measured. The dependence of this current on bias voltage (i.e., on beam energy) should correlate with the electron surface reflectivity. The current rapidly approached zero when the bias voltage was close to the electron-gun energy, verifying that the primary energy of the gun was 13.5 eV. The unfocused beam had a spot size larger than the sample surface, as determined by changes in the sample current as a function of sample position. The total beam current of ~0.36 μA was the sum of the sample current and the reflected beam current measured on the CMA's cylinders. Neither the total beam current nor the beam size showed any significant dependence on the sample bias voltage, and 0.36 μA has been used to calculate the electron flux incident upon the surface for all bias voltages. The incident electron energy was controlled by the sample bias voltage. The beam energy was 1, 2, 5, and 8 eV with respect to the sample vacuum level when the bias was -12.5, -11.5, -8.5, and -5.5 V, respectively.

Clean InP(110) surfaces were obtained by cleavage of n-type ($N_d=2\times10^{18}$ cm^{-3}) InP posts at 30 K at pressures below 1×10^{-10} Torr. Two-Langmuir (1 L$=1\times10^{-6}$ Torr sec) O_2 was exposed to the surface at 30 K before electron irradiation, and a valence-band energy-distribution curve (EDC) was taken with $h\nu=40.8$ eV to serve as a reference. The O_2-covered surface was irradiated for a short period for each electron energy and the valence-band spectrum was acquired after each exposure. This procedure was repeated until the O_2 emission features were no longer observed in the EDC's. The sample was then warmed to ~70 K to desorb any remaining O_2, and valence-band and core-level spectra were again measured.

In Fig. 1 we show a series of valence-band EDC's for

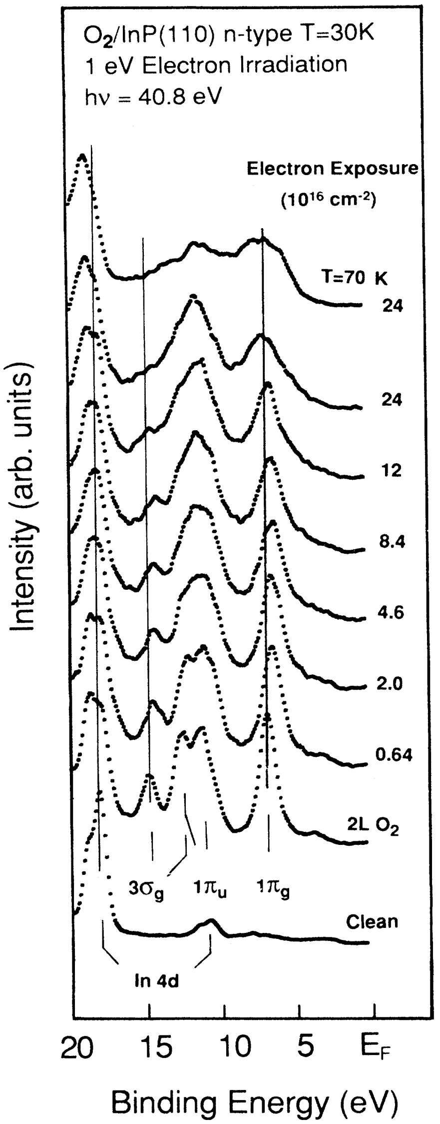

FIG. 1. Valence spectra of InP(110) before and after 2 L-O_2 physisorption and as a function of 1-eV electron irradiation. The electron exposures are given on the right-hand side.

molecular oxygen condensed on InP(110) as a function of 1-eV electron irradiation. These curves are shown in arbitrary intensity units and are not normalized with respect to one another. The electron exposure was determined from the total electron beam current (0.36 μA), the time of each exposure, and an approximate sample surface area of 0.1 cm^2. The clean-surface EDC at the bottom reveals the In $4d$ doublet at $\sim$18-eV binding energy, excited by $h\nu$=40.8 eV. The same In $4d$ core level also appears at higher kinetic energy (with apparent binding energy of $\sim$10.5 eV) due to a He line at $h\nu$=48.4 eV. The valence-band features themselves are much weaker. The EDC for the O_2-covered surface clearly shows emission from the oxygen molecular orbitals, as labeled.[8] They are derived mainly from O $2p$ levels. A level derived from O $2s$ overlaps with an In $4d$ core level near $\sim$18 eV, as is evident from its change in shape. During electron irradiation, emission from the O_2 orbitals is progressively reduced and the broad oxide features with binding energies of $\sim$7 and $\sim$11 eV become stronger.[9] Emission from the $3\sigma_g$ orbital near 14.8 eV eventually disappeared for high electron exposure. Its intensity can serve as a measure of the presence of O_2 on the surface because it does not overlap with the broadened valence-band oxide feature. The In $4d$ core-level peak at $\sim$18 eV also broadened as a result of oxide formation. The top EDC of Fig. 1 was taken after warming the sample to 70 K, and it clearly shows extended surface oxidation and the absence of O_2.[9]

In Fig. 2 we show EDC's that summarize the valence-band evolution of condensed O_2 on InP(110) during irradiation with 8-eV electrons. The progression is very similar to that for 1-eV irradiation except that the exposure needed to produce an equivalent stage of reaction is much less. For irradiation with 2- and 5-eV electrons (spectra not shown), the evolution is again similar, with differences that reflect the total electron exposure.

P $2p$ core-level spectra were also acquired for the fully reacted surface after it was irradiated with electrons. They were taken after the reaction had saturated at 30 K and residual O_2 had been desorbed by warming to 70 K,

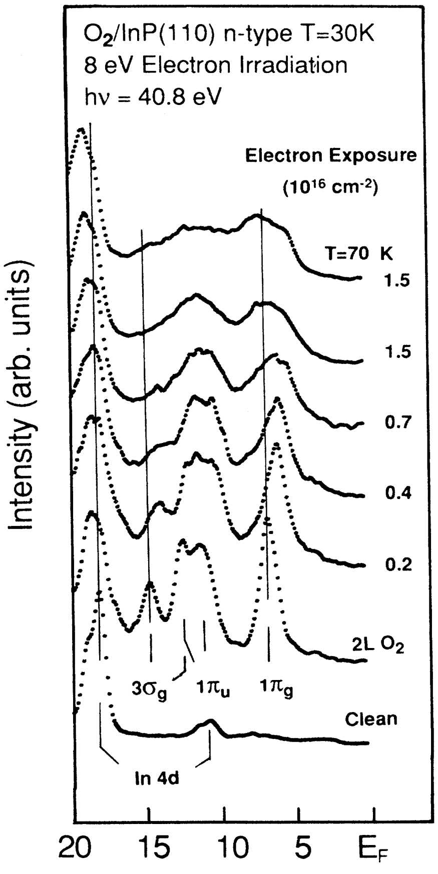

FIG. 2. Valence spectra of InP(110) before and after 8 L-O_2 physisorption and as a function of 8-eV electron irradiation, as in Fig. 1.

thus excluding any x-ray-activated reaction. A chemical shift of ~4.5 eV for the oxide relative to the clean surface clearly demonstrates that the surface was strongly oxidized.[9–11] Comparison with the results of Hughes and Ludeke,[10] with account taken of differences in surface sensitivity, suggests that the amount of oxide grown is approximately one monolayer. We conclude that the electron-beam-induced changes in the valence band are associated with surface-oxidation reactions rather than desorption of O_2. While the latter may also occur, it is not the dominant process in the low-O_2-coverage regime, consistent with results for photon-enhanced oxidation that showed desorption was only important when excess oxygen decorated a fully reacted overlayer.[6]

The reaction cross sections plotted in Fig. 3 were determined from our data in the following manner. Since the O_2 $3\sigma_g$ molecular orbital (at ~14.8 eV) does not overlap with oxide features, the decrease of its intensity as a function of electron exposure was used to characterize the surface reaction. This was fitted to an exponential decay function $e^{-\gamma E}$, where γ is the reaction cross section and E is the electron exposure. The best fit yielded a reaction cross section of 8×10^{-18} cm^2 for 1-eV electrons. For different electron energies, the intensity change in the $3\sigma_g$ emission at ~14.8 eV was again used to quantify the reaction speed. The spectra chosen in this manner for different electron energies are in fact very similar in shape to each other, which further show the consistency of the procedure. The cross sections are derived for 2-, 5-, and 8-eV electrons as 1×10^{-17}, 8×10^{-17}, and 2×10^{-16} cm^2, respectively.

The experimental data clearly show a very strong energy dependence of the reaction cross section for electron-stimulated oxidation of InP(110) at low temperature (Fig. 3). This energy dependence and the magnitude of the cross section are very similar to what has been reported for electron attachment on O_2 via the negative-ion resonant states. Such negative-ion formation has been well studied for gas-phase O_2 molecules[12] and has been investigated for condensed O_2 as well.[13] In this attachment process, the incoming electron is trapped temporarily in the resonant state of O_2^-. For gas-phase O_2 the maximum cross section for formation of this resonant state is about 1×10^{-16} cm^2 for 7.8-eV electrons and it is very small for electrons with energies less than 4 eV.[14] A major decay channel of the resonant state is via *autoionization,* which leaves O_2 in excited-state configurations.[13,14] Another decay channel involves dissociative formation of O and O^- with a maximum cross section of 1.3×10^{-18} cm^2 for gaseous O_2 and 2×10^{-17} cm^2 for condensed O_2 (Ref. 13). The surface-reaction cross sections measured in here for O_2/InP(110) agree very well with those for the resonant-state formation of O_2^- in their energy dependence and in magnitude, demonstrating the importance of this resonant state as an intermediate stage in electron-induced surface processes. The decay of the resonant state via autoionization produces highly reactive excited-state species. We note that excited O_2 produced by hot filaments during oxygen exposure are significantly more reactive than ground-state O_2 as far as surface oxidation is concerned.[11] We also note that the cross section for dissociative decay of the resonant states and production of O and O^- is too small to account for the observed reaction rate.

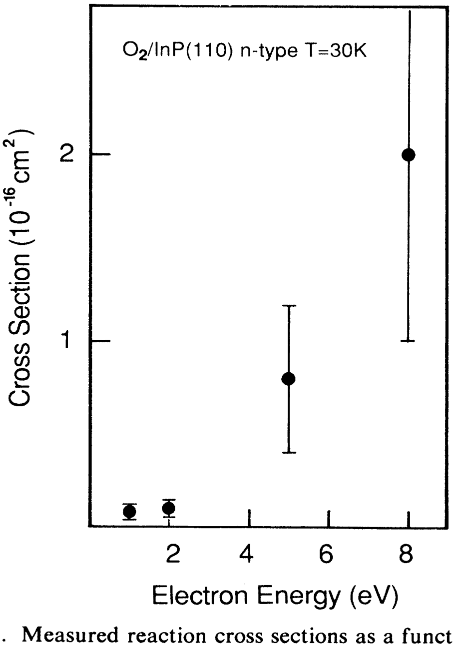

FIG. 3. Measured reaction cross sections as a function of the kinetic energy of the incident electrons for O_2/InP(110) at 30 K.

The fact that the reaction cross section for 1- and 2-eV electrons is not negligible is interesting because the cross section for the resonant-state formation for isolated O_2 molecules is negligible at these energies.[12] However, when O_2^- is condensed on a substrate that has an appreciable dielectric constant, an image charge is formed to attract O_2^- toward the surface. In such an attractive potential, the maxima in the resonant-state formation cross section tend to broaden and shift to lower energy.[13,15,16] Indeed, Demuth, Schmeisser, and Avouris[17] have directly observed this downward shift and broadening for O_2 condensed on Ag. It may be that the tail of the resonant peak near 6–8 eV for gas-phase O_2 becomes appreciable in the 1–2-eV region and thus would account for the reaction observed here.

The electron energies in our experiment are too low to produce significant numbers of secondary electrons but they can produce electron-hole pairs. Photoenhanced oxidation of semiconductor surfaces has been attributed to such pair production.[18–20] During electron-beam irradiation, pair production is mainly due to electrons absorbed by the substrate, and the number of such electrons has been monitored during electron exposure in our experiments. To produce a similar degree of surface oxidation, the total of absorbed 1-eV electrons is ten times that of 8-eV electrons. For InP, the energy available for 1- and 8-eV electrons to produce electron-hole pairs are 5.4 and 12.4 eV, respectively, because the proper energy reference is the conduction-band minimum which is 4.4 eV below vacuum level.[21] If the reaction rate was linearly proportional to the number of electron-hole pairs, to produce a similar degree of surface oxidation the absorbed 1-eV electrons should be two to three times larger than that of

8-eV electrons. This is smaller than what we measured. Thus we conclude that processes related to electron-hole pairs are not dominant reaction channels here.

In conclusion, we have observed that 1-8-eV low-energy electrons induce strong oxidation on the O_2-condensed InP(110) surface at 30 K. The reaction cross sections are measured and reveal a strong energy dependence. We demonstrate the importance of O_2^- negative-ion resonant-state formation in the surface processes induced by low-energy electrons.

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