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Electron-stimulated desorption of O^+ ions from a gas-covered CdS(0001) surface

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Electron-stimulated desorption of O^+ ions from a CdS(0001) single-crystal surface exposed to O_2 and NO has been investigated. Only O^+ desorption was observed in both cases with a total cross section of $\sim 10^{-17}$ cm^2. The dependence of the ion yield on the incident electron-beam energy from 0–180 eV exhibits thresholds at both the Cd $4d$, $4p$, $4s$, and the S $3s$ and $2p$ core-level binding energies. Evidence is presented which indicates that the ions may originate from multiple states.

INTRODUCTION

Most electron-stimulated-desorption (ESD) investigations have focused on the surfaces of elemental metals, rather than compounds or alloys. Useful insight into the desorption process might be obtained by comparison of the ESD of several different ionic species from the surface of a material in which there is the possibility of adsorbate bonding to more than one chemical element. Wurtzite CdS is ideal in this regard. Furthermore, since CdS is a wide-band-gap semiconductor ($E_g = 2.48$ eV), reneutralization effects might be expected to be less important in the desorption of ions than for a metallic substrate.[1]

The aim of the work reported here is to investigate surface bonding of species to semiconductors through ESD studies from the CdS(0001) surface exposed to O_2 and NO.

EXPERIMENTAL PROCEDURE

The experiments were undertaken in a stainless-steel ultrahigh-vacuum system. The experimental setup has been described in Ref. 2 and consists of a single-pass cylindrical-mirror analyzer (CMA), quadrupole mass spectrometer (E.A.I. Quad 150 A) for monitoring the desorbing species, and a low-energy electron gun. The vacuum system was also enclosed by Helmholtz coils which were used to bring the magnetic field in the vacuum system to a minimum (< 10 mG).

SAMPLE PREPARATION

The sample used, a CdS(0001) single crystal, was first polished to optical flatness using 0.05-μm Buehler solution, and then cleaned with acetone and methanol in an ultrasonic cleaner. The major surface contaminants of the sample when freshly installed into the vacuum system were carbon and oxygen. Cleaning of the sample surface was accomplished by a series of 2.5-keV argon-ion bombardments, followed by anneals in $\sim 3\times 10^{-10}$ Torr vacuum at 500 °C for 15 min.

ADSORPTION OF GASES

Oxygen exposure

Oxygen adsorption on CdS(0001) surfaces has been the subject of a large number of investigations.[3–11] Dark conductivity, photoconductivity,[4–7] and photovoltage[12] have been found to depend strongly upon oxygen adsorbed on the CdS surface.

The atomically ordered and clean CdS surface has been found to be insensitive to O_2 exposure.[8,10,11] Lichtensteiger, Webb, and Lagowski[11] have shown that the nonreactive surface exhibits a significant rate of O_2 adsorption only upon irradiation with electrons in the presence of water vapor. This was shown to be as a result of local activation of the surface rather than the dissociation of previously adsorbed species. They showed that during the initial stages of adsorption, oxygen preferentially bonded to S atoms, but further electron irradiation resulted in the oxidation of CdS, with an increasing amount of oxygen bonded to Cd atoms. On the polar (0001) clean surface, Campbell and Farnsworth[12] found no observable adsorption without photoirradiation. The sticking coefficient of O_2 on the (0001) surface was found to less than 10^{-13} in the dark. However, visible illumination increased this to between 10^{-11} and 10^{-12} for the (0001)Cd-terminated surface and 10^{-9} to 10^{-10}, for the faceted (0001)S-terminated surface. Also, Miller and Haneman[13] observed oxygen adsorption on the (0001) surface at 77 K only with photoillumination of the surface.

In the present oxygen-adsorption attempts, no O Auger-electron-spectroscopy (AES) peak was detected even under photoirradiation of a clean, annealed CdS(0001) surface exposed to $\sim 10^8$ L (1 L = 1 langmuir = 10^{-6} Torr sec) of oxygen. The CdS surface was then exposed to 2.5-keV argon ions at a dose of 1×10^{15} ions/cm^2, thus creating surface damage. Exposure of this damaged surface to O_2 at 5×10^{-2} Torr and under photoirradiation from a 5-kw xenon discharge lamp resulted in adsorption of oxygen. Figure 1 shows the AES spectrum of CdS after photoinduced adsorption of research-

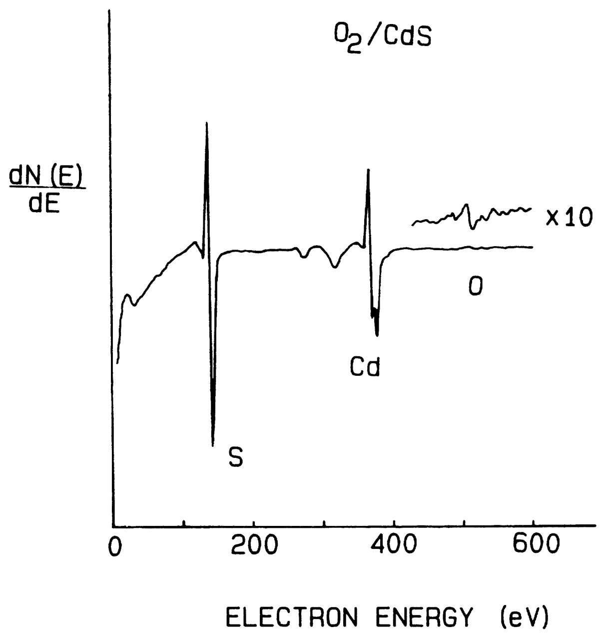

FIG. 1. Auger spectrum of CdS after exposure to ~10^8 L of O_2.

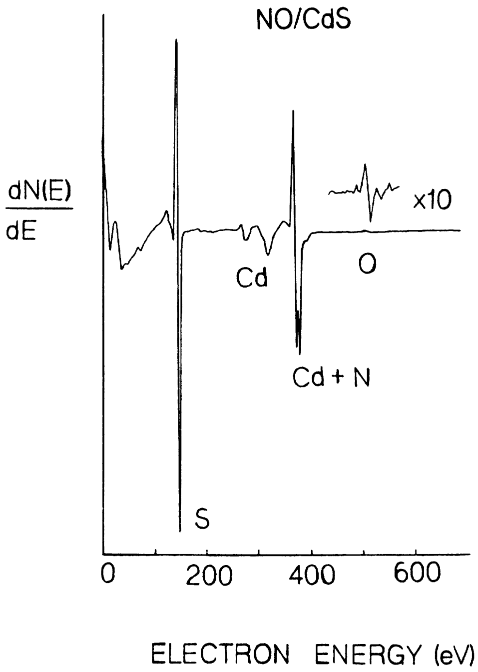

FIG. 2. Auger spectrum of CdS after exposure to ~10^8 L of NO. The N AES peak overlaps the Cd 382-eV peak.

grade oxygen on the ion-damaged surface exposed to ~10^8 L of oxygen.

Nitric oxide exposure

There have been no previous studies of nitric oxide (NO) chemisorption on CdS. However, N_2O adsorption on CdS has been studied by Mark.[14,15] Since NO has been reported to interact strongly with stainless steel,[16] the vacuum system was first passivated by ~10^3 L of NO as suggested by Bermudez.[17] In similarity to O_2 exposure, NO exposure resulted in no observation of N or O AES signals either for the clean, annealed CdS sample or under photoirradiation. Ion bombardment of the CdS surface, however, resulted in NO adsorption. Figure 2 shows the AES spectrum after photoinduced adsorption of NO on the clean, damaged CdS surface exposed to ~10^8 L. The N AES peak overlaps the Cd 382-eV peak.

After the gas exposures, the pressure in the chamber was brought to the low-10^{-10}-Torr range prior to undertaking electron-stimulated-desorption measurements. This minimized the possibility of excitation of molecules in the gas phase and possible readsorption. Electron irradiation was accomplished using a low-energy electron gun of current density $J \sim 20$ $\mu A/cm^2$. The sample was positioned such that the gun and the mass spectrometer each made an angle of ~22.5° with the sample surface normal. With the external Helmholtz coils adjusted for minimum magnetic field, the incident-electron-beam current was measured and used to normalize the ion yield detected by the mass spectrometer. With the electron energy fixed, the decrease in desorption current for the desorbing species was measured as a function of time. All measurements were done at room temperature.

RESULTS AND DISCUSSIONS

The desorption, normalized to the incident-electron current, versus the electron energy are shown in Figs. 3 and 4 for the two adsorbates O_2 and NO. The electron energy has been corrected for the work function of the tungsten filament (4.5 eV). ESD from CdS exposed to O_2 and NO resulted in the observation of only O^+ ions. There was no N^+ desorption from NO-exposed sample within our sensitivity (~10^{-13} Torr partial pressure).

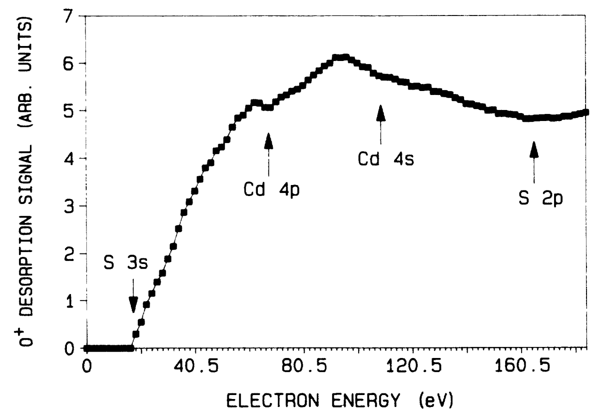

FIG. 3. O^+ desorption signal vs incident electron energy (corrected for the work function of tungsten filament) for CdS preexposed to O_2. Arrows indicate core levels of Cd and S within the specified energy range.

This is consistent with ESD studies on Si(111) (Refs. 18 and 20) and GaAs(100) (Ref. 2) where N^+ desorption was also not observed.

Energy thresholds in Fig. 3 for O^+ ESD from the O_2/CdS system can be seen at 16.5±0.6, 68.5±0.6, and 160.5±0.6 eV. These are approximately coincident with the S 3*s* (17 eV),[21] Cd 4*p* (68 eV),[21] and S 2*p* (162–166 eV) (Refs. 11 and 21) core-level ionization potentials. The absence of Cd 4*d* (11 eV) core-level excitation should be noted in Fig. 3. Since deeper core levels were excited, it is probable that the Cd 4*d* core level was equally excited, but the signal could not be resolved above the noise level. Energy thresholds in Fig. 4 for O^+ ESD from the NO/CdS system can be seen at 12.5±0.6, 18.5±0.6, 66.5±0.6, 110.5±0.6, and 160.5±0.6 eV. These are approximately coincident with the Cd 4*d* (11 eV),[21–23] S 3*s* (17 eV),[21] Cd 4*p* (68 eV),[21] Cd 4*s* (109 eV),[21] and S 2*p* (162–166 eV).[11,21] It should be noted that enhanced desorption of O^+ was observed under excitation of *both* the Cd and S core levels in Figs. 3 and 4.

The total cross section for ESD characterizes the probability of removal of a specie from a particular state. This removal process includes the desorption of neutral, metastable, ionic species, etc. Total cross sections for the desorbing species were obtained using the standard signal-decay method in which the decay constant is obtained from semilogarithmic plot of the ion signal versus time.[24] Figures 5 and 6 show semilogarithmic plots of O^+ yields for the O_2/CdS and NO/CdS systems, respectively. It is seen that the plots cannot be characterized by a single decay constant. This result is similar to the work of Lagowski, Lichtensteiger, and Williams[10] for O_2/CdS and Craig and Hock[25] for CO/PT, where they found that O^+ cannot be characterized by a single decay constant. As a result, there are two values for the O^+ total cross section from CdS. This fact, together with the increase in ion yields at the excitation of both Cd and S core levels indicate that perhaps the O^+-ion signal originates from two states, e.g., that on the CdS(0001) surface the oxygen is bonded to both Cd and S. This is consistent with the work of Lichtensteiger and co-workers[11] where they reported oxygen to be bonded to both Cd and S at high exposures.

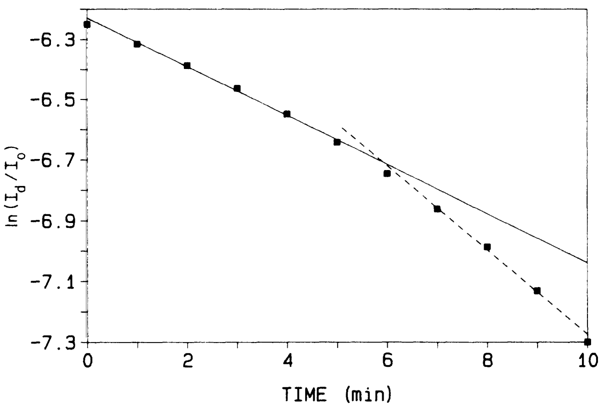

FIG. 5. Semilogarithmic plot for O^+ ESD yield at 100-eV electron energy from CdS preexposed to O_2. This yield cannot be characterized by a single decay constant.

Wurtzite CdS(0001) consists of double layers of atoms. The atoms in a single layer (made up of either Cd or S atoms) are triply bonded to the atoms in the closest neighboring layer and only singly bonded to the more distance layer.[12] The oxygen sticking coefficient on the (0001)S-terminated surface is known to be higher than that of Cd-terminated surface by about an order of 2.[12] Therefore, it is expected that oxygen will be more strongly bonded to S than to Cd. Hence, the O^+ depletion shown in Fig. 5 shows up as initial O^+ desorption principally from S atoms (smaller cross section) followed by mainly desorption from the Cd atoms. Since CdS consists of double layers of Cd and S, this implies that the topmost layer of our sample is made up of mainly S atoms. This is consistent with our CdS sample being supplied as S terminated.

From the similarity of Figs. 5 and 6, it is likely that the S- and Cd-terminated faces also exhibit different sticking coefficients for NO. Hence the initial O^+ desorption is

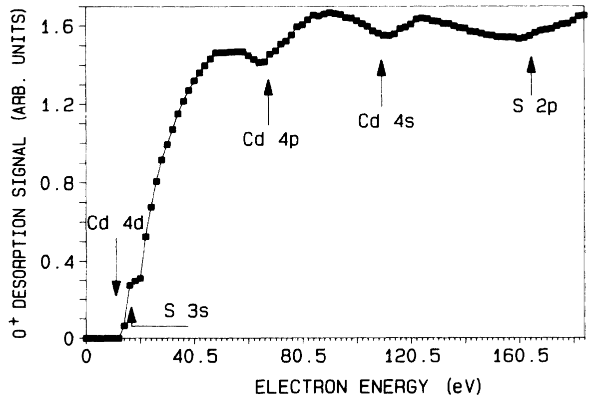

FIG. 4. O^+ desorption signal vs incident-electron energy (corrected for the work function of tungsten filament) for CdS preexposed to NO. Arrows indicate core levels of Cd and S within the specified energy range.

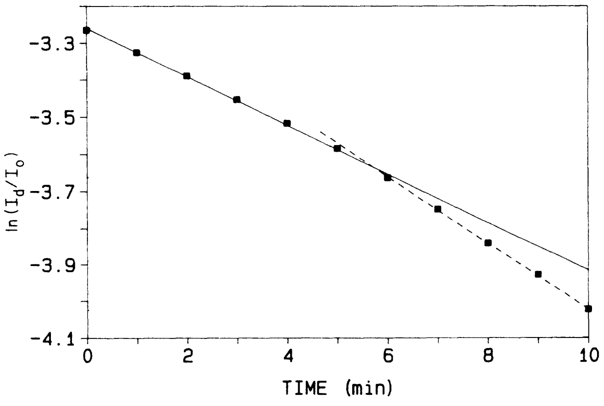

FIG. 6. Semilogarithmic plot for O^+ ESD yield at 100-eV electron energy from CdS preexposed to NO. This yield cannot be characterized by a single decay constant.

principally from oxygen bonded to the S atoms with the secondary desorption mainly from Cd atoms. The total ESD cross sections for O_2/CdS are 1.06×10^{-17} cm^2 (S-atom bonding) and 1.79×10^{-17} cm^2 (Cd-atom bonding) (see Fig. 5), while for the NO/CdS (Fig. 6) the total cross sections are 1.48×10^{-17} cm^2 (S-atom bonding) and 2.02×10^{-17} cm^2 (Cd-atom bonding). It should be noted that the O^+ total cross sections from O_2/CdS are lower than those from NO/CdS. This indicates that NO is more weakly chemisorbed on the CdS surface than O_2. This is similar to the work of Bermudez[17] for GaAs(110), where the NO sticking coefficient was found to be smaller than that of O_2 by a factor of 20–100. The high values of the total cross sections indicate a rather weakly chemisorbed nature of the adsorbed species.[24,26] This is probably true if we recount that no appreciable adsorption was obtained, except when the CdS surface was ion damaged.

ESD has been described by Menzel, Gomer, and Redhead[27,28] (MGR model), and also by Knotek and Feibelman[29] (KF model) for maximal valency and ionic systems. An extension or generalization of the KF model[29] to covalent and nonmaximal valency systems is the Auger-stimulated desorption (ASD).[30,31] The ASD model assumes an intra-atomic Auger decay of a core hole, followed by desorption via a localized two-hole state. A necessary condition for the ASD model is the localization of the two-hole state, a condition necessary to provide the Coulomb repulsion for the expulsion of the ion.[32] CdS is a nonmaximal valence system, and its bonding with the adsorbates O_2 and NO is very likely covalent. The ionization of the band of Cd 4*d*, 4*p*, 4*s* and S 3*s* and 2*p* states lying below the valence-band edge is hence followed by autoionization[20,33,34] to give the various states, with two or more holes in the valence band, leading to desorption.

From the thresholds and hence the core levels excited, it seems that the ASD model is applicable to our O_2/CdS and NO/CdS systems.

CONCLUSIONS

ESD from CdS exposed to O_2 and NO shows desorption of O^+ as a result of excitation of Cd and S core levels for the nonmaximal valence CdS system. From the core-level excitation thresholds, it is concluded that oxygen from O_2 and NO is bonded to both Cd and S. The total desorption cross section for O^+ shows a two-state behavior with values of 1.06×10^{-17} and 1.48×10^{-17} cm^2 (for O_2 and NO exposures) for desorption from the S surface and 1.79×10^{-17} and 2.02×10^{-17} cm^2 (for O_2 and NO exposures) for desorption from the Cd surface, with the high values portraying the weakly chemisorbed nature of the adsorbed species.

ACKNOWLEDGMENTS

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