Sodium or cesium-assisted nitrogen monoxide reaction with InP(110) at ambient temperature

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We investigate by means of core-level and valence-band photoemission spectroscopies with synchrotron radiation to what extent nitridation and oxidation of InP(110) can be promoted, at ambient temperature, using cesium or sodium alkali metal catalyst and pure nitrogen monoxide gas. We confirm that cesium has a better catalytic activity in InP oxidation than sodium. Compared to molecular oxygen, the weaker bond strength of the nitrogen monoxide molecule favors the oxidation of InP using sodium as electronic promoter. However, both alkali metals are inefficient to induce a detectable reaction between nitrogen and InP for NO exposures up to 1000 L (1 Langmuir (L) = 10^{-6} Torr.s).

1. INTRODUCTION

The realization of a reliable InP metal - insulator - semiconductor structure depends strongly on the ability to develop an appropriate passivation process for the InP surface. Exposures as high as 10^{12} L of the InP(110) surface to molecular or excited oxygen are necessary to observe substantial oxidation of the semiconductor at ambient temperature [1-2]. However, it has been recently shown that an alkali metal like cesium (or potassium) is an efficient electronic promoter of oxidation (or nitridation) of InP(110). Indeed, catalytic oxidation [3-4] (or nitridation [5]) of InP(110) can be achieved at ambient temperature by overlayer deposition of Cs (or K) and subsequent exposure to O₂ (or N₂). In this case, the oxidation extent, at ambient temperature, increases by as much as 13 orders of magnitude. But, the Cs/InP interface is inefficient in promoting InP nitridation for N₂ exposures up to 4000 L [5]. The same is true for the Na/InP interface where oxidation by means of molecular oxygen is not observed for exposures up to 116 L [4]. Since the NO bond strength is smaller than that of N₂, it is challenging to investigate to what extent nitridation and oxidation of InP can be promoted at ambient temperature using Cs or Na alkali metal catalysts and pure NO gas.

2. EXPERIMENTAL

The core-level and valence-band photoemission experiments were performed in an ultra-high vacuum system at a pressure better than 5×10^{-11} Torr at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Details of the experimental techniques and apparatus have been reported elsewhere [6]. The radiation emitted by the 1 GeV "Aladdin" storage ring was dispersed by a 6m toroidal grating monochromator. The photoelectron energies were discriminated by an angle-integrating double-pass cylindrical mirror analyzer. The overall resolution energy was 0.48 eV (photon energy = 82 eV, In 4d core-levels and valence-band spectra) or 0.55 eV (photon energy = 170 eV, P 2p core-levels). The InP(110) surfaces were prepared by *in situ* cleaving of a n type-InP(110) single crystal rod. The depositions of Cs or Na were done using SAES Getters chromate sources up to a certain coverage in the submonolayer range, which is estimated as ~ 0.7 monolayer (ML) (1 ML corresponds to $\sim 5 \times 10^{14}$ atoms cm⁻²). Then, the alkali metal (Cs or Na)-covered InP surfaces were exposed to various introductions of NO gas up to 1000 L. Data

acquisition started within few minutes after the alkali metal deposition and after each exposure to NO.

3. RESULTS AND DISCUSSION

The reaction between NO and the alkali metal-covered InP surfaces was investigated *in situ* by P 2p and In 4d core-levels and valence-band spectra analyses.

3.1 Core-levels analysis

The alkali metal-submonolayer deposition induced the creation of positive kinetic energy (KE) shifts (0.48 eV (Cs) or 0.45 eV (Na)) of the core-level P 2p and In 4d lines (figure 1). KE shifts of 0.7 to 0.8 eV have been measured after deposition of 1 ML of alkali metal atoms [3-5]. These shifts are the result of the evolution of the substrate band bending upon alkali metal deposition [3-4]. In addition, the P 2p and In 4d line shapes were well fitted if a new component was added on the low KE side of the bulk component at $0.4 \text{ eV} \pm 0.1 \text{ eV}$ (P 2p) or $0.8 \text{ eV} \pm 0.1 \text{ eV}$ (In 4d). This is shown in figure 2 for the P 2p core-level, where this component is labelled I (B and S are respectively the bulk and surface P 2p components). After deposition of Cs, the integrated intensity ratio $I/(I+B+S)$ is greater, by a factor of ~ 4 , than the ratio measured for Na

Figure 1: P 2p and In 4d core-levels spectra after deposition of a submonolayer of Na (a, b) or Cs (c, d), and subsequent exposures to 0.1 L and 1000 L of pure NO gas.

deposition. The same behavior is observed for the In 4d core-level (not shown), where the corresponding factor is ~ 1.5 . The I component could be due to an alkali metal-induced local interface state and/or to some electronic charge transfer between the InP surface and the alkali metal overlayer. This component cannot be the signature of elemental P at the interface, since the measured KE shift ($0.4 \text{ eV} \pm 0.1 \text{ eV}$) is smaller than the expected value of $1.1 \text{ eV} \pm 0.1 \text{ eV}$ [7].

Figure 2: Curve fitting of the P 2p core-levels of the clean InP(110) surface (a), after deposition of a submonolayer of Cs (b) and subsequent exposure of 1000 L to NO gas (c). The curve fitting parameters are: Gaussian width = 0.55 eV, spin-orbit splitting = 0.86 eV, branching ratio = 1.97 and Lorentzian width = 0.078 eV. These parameters were kept constant for the entire set of fittings.

As shown in fig.1, the KE shifts induced by cesium or sodium deposition were reduced progressively upon exposure to NO gas. A minimum exposure of ~ 100 L was necessary in order to observe a significant reaction of NO with the Na-covered InP surface. On the contrary, an exposure as low as 0.1 L was sufficient to detect a 4.4 eV P 2p chemical shift to lower KE from the P 2p substrate line (fig.1.c) and a broadening of the In 4d level which changed shape for an exposure of 1000 L (fig. 1.d). Upon exposure to NO, the relative intensity of the P 2p component labelled I (fig. 2) vanished more rapidly than the B and S components and practically disappeared after an exposure of 1000 L. At this last step, the intensities of the B and S components were faint, but still present. The above results are consistent with an oxidation of InP(110) with the formation of P-O and In-O bonds [1, 3-4, 7]. Indeed, the characteristic 1.8 eV P 2p chemically shifted line [5], corresponding to the formation of P-N bonds, was not observed. From our data we cannot presently deduce the atomic composition of the thin oxide layer. In the case of InP, equilibrium thermodynamics predicts thermal oxides to be made only of InPO_4 [7]. The other compounds of the In-P-O system are In_2O_3 , P_2O_5 and $\text{In}(\text{PO}_3)_3$. Curve fitting of the oxide P 2p chemically shifted line can be achieved using mainly three components labelled O1, O2 and O3 (fig. 2.c). They are shifted by 4.7 eV, 4.1 eV and 3.6 eV respectively to lower KE from the B substrate component. This result can be interpreted by the existence of mainly three different chemical environments for P in the thin oxide layer. In any case, our experimental results confirm that cesium has a better catalytic activity in InP oxidation than sodium. Here, the weaker bond strength of the NO molecule favors the appearance of a P 2p chemically shifted peak at an exposure of 100 L of NO gas, whereas it was impossible to observe it for exposures up to 116 L using molecular oxygen [4]. However, both alkali metals are inefficient to induce a detectable reaction between nitrogen and InP.

3.2 Valence-band spectra analysis

The Fermi level of the clean InP(110) surface covered with a cesium or sodium overlayer is chosen as a reference for the binding energies (BE) given below. The valence-band spectra (fig. 3) of the Na- or Cs-covered InP surface are mainly characterized by an electronic structure located at a BE of ~ 6 eV, which has

been previously interpreted as due to an alkali metal-induced interface state [4]. The exposition of these surfaces to NO led to a drastic change of the valence-band spectrum of the Cs-covered InP surface. Two new peaks labelled L and J (fig. 3.b) appeared at a BE of 5.3 eV and 8.2 eV respectively, and their intensity increased with increasing NO exposure. They correspond to the formation of atomic oxygen and are related to non bonding and bonding O 2p states respectively [4]. The expected signature of N 2p states from atomic nitrogen at a BE of 6 eV [5] was hardly detectable.

Figure 3: Valence-band spectra of the InP(110) surface after deposition of a submonolayer of Na (a) or Cs (b), and subsequent exposure of 1000 L to NO gas.

4. CONCLUSION

The reaction at ambient temperature of NO with cesium- or sodium-covered InP(110) surface has been studied by means of core-level and valence-band photoemission spectroscopies with synchrotron radiation. We confirm that cesium has a better catalytic activity in InP oxidation than sodium. Moreover, we observe that the weaker bond strength of the NO molecule, as compared to molecular oxygen, favors the oxidation of InP using sodium as electronic promoter. However, both alkali metals are inefficient to induce a detectable reaction between nitrogen and InP for NO exposures up to 1000 L.

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