Electronic Reconstruction at a Buried Ionic-covalent Interface Driven by Surface Reactions

Chung-Ting Luo (羅中廷)[2], Hao-Dau Li (李宏道)[1],
Jeng-Yang Chung (鐘仁陽)[1], and Deng-Sung Lin (林登松)[2]

[1]Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan
[2]Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan

We report the discovery of a much more dramatic effect under a well-controlled experimental condition periodic switching of the electronic structure and bonding character at a buried interface during the cyclic growth in a thin ionic film. Specifically,this work investigates the formation and evolution of interfacial bonding in NaCl growth on Ge(100). The choice of NaCl is partially motivated by its prototypical ionic behavior and its close lattice matching with Ge(5.63 vs5.65 Å). In addition, NaCl can be grown on Ge(100) layer by layer in cycles of sequential half reactions HRs that involve the adsorption of Cl (Cl-HR) and Na (Na-HR) as shown in Fig.1. This process is unlike the typical growth in alkali halides that is based on molecular-beam epitaxy (MBE) using ionically balanced molecular units.The sequential HRs in this case yield additional information; the buried interface exhibits large oscillations of bonding character van der Waals vs ionic that are governed by whether the growing film is ionically balanced or contains an extra layer of Cl. Therefore,film growth in our case, as a surface event, exerts a long-range influence on the chemistry of the interface.

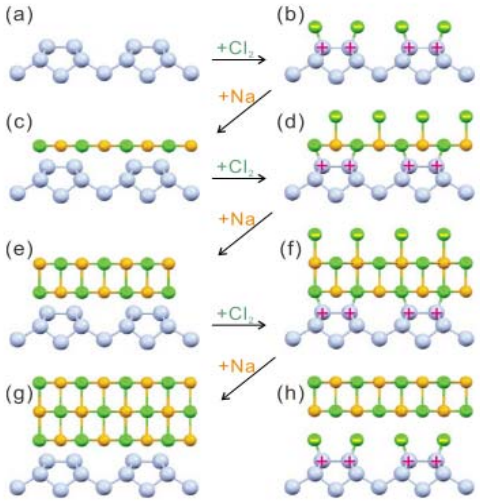

Fig. 1: (Color online) (a)-(g) Simplified models for various stages of growth in NaCl on Ge(100).The smallest, the middle, and the the largest spheres represent Na, Cl, and Ge, respectively. Some of the atoms are marked with positive and negative signs to indicate their nominal ionic states. (h)Alternate model to (f), obtained after the growth of two full layers of NaCl and an extra Cl-HR.

Figure 2(a) presents Ge 3d and Na 2p core-level spectra.The Ge 3d spectrum of the clean surface shows a bulk component(B) and a surface-shifted (−0.44 eV) component (S);the latter is associated with the Ge atoms in the top layer.16,18Here, the relative binding-energy scale is referenced to the bulk Ge 3d5/2 position (29.5 eV relative to the valence-band maximum). This energy-referencing scheme eliminates any shifts due to changes in band bending. Figure 3(a) shows the measured binding energy of the Ge 3d5/2 B component relative to the Fermi level at various stages of sample growth; it varies by ~0.34 eV due to changes in surface band bending.

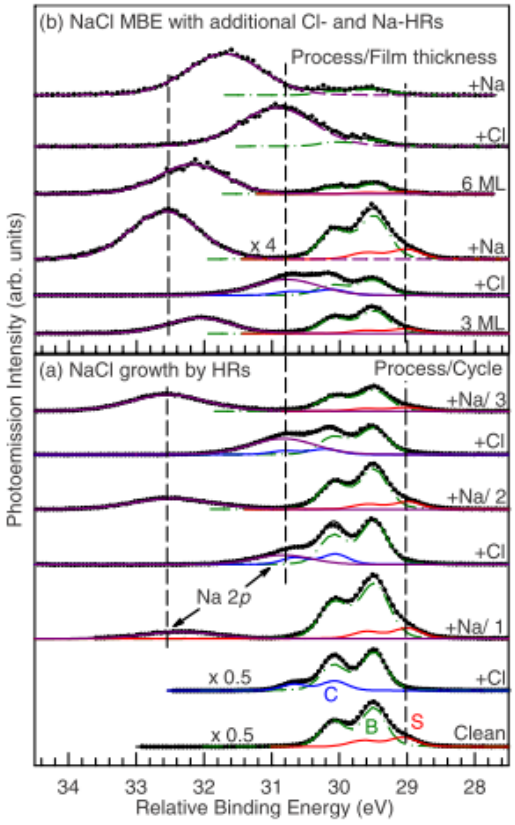

Fig. 2: Color online Ge 3d and Na 2p core-level photoemission spectra obtained in various growth stages.

A surprisingly electronic reconstruction at a buried NaCl-Ge(100) interface is observed during cyclic half reactions.Periodic switching between ionic bonding and van der Waals bonding at the interface is evident from the measured core-level shifts. The large long-range chemical and electronic coupling can be attributed to a strong electrostatic interaction associated with the high ionicity of NaCl. The implication that lattice distortions or ionic motions minimize the electric-field energy during the alternative adsorption of anions and cations suggests an interesting avenue for materials engineering. The findings in this investigation may have important implications for nanomaterials and devices with dielectric-covalent junctions.