Characterization of buried thin films with resonant soft x-ray fluorescence

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The geometric and electronic structure of a buried monolayer of boron nitride (BN) has been probed using resonant soft x-ray fluorescence (SXF). By using the strong $\pi^*$ resonance feature in the resonant fluorescence spectrum near the $B$ (1s) threshold, we were able to detect the BN thin film and examine changes in its electronic structure when the monolayer is placed between different materials. Our results demonstrate the capability of the resonant SXF technique for probing the element-specific electronic structure of a buried thin film nondestructively. © 1995 American Institute of Physics.

The atomic-scale properties of buried thin films and interfaces have been and will remain a subject of intense investigation. In many instances these properties have been probed by photoemission and other surface sensitive techniques via monolayer deposition of the materials. However, in recent years the applicability of these results to the true interface or thin film as it exists after many layers are deposited has been questioned in some systems. X-ray diffraction has been used to probe the atomic structure of buried interfaces, and when combined with x-ray absorption can provide some chemical information. In this Letter we demonstrate the capability of resonant soft x-ray fluorescence for probing the electronic and geometric structure of buried thin film systems which are difficult if not impossible to probe using other techniques.

Soft x-ray fluorescence (SXF) spectroscopy using synchrotron radiation offers several advantages over surface sensitive spectroscopies for probing the electronic structure of complex multi-elemental materials. Due to the long mean free path of photons in solids ($\sim$1000 Å), SXF is a bulk-sensitive probe. Also, since core levels are involved in absorption and emission, SXF is both element- and angular-momentum selective. SXF measures the local partial density of states (DOS) projected onto each constituent element of the material. The chief limitation of SXF has been the low fluorescence yield for photon emission, particularly for light elements. However, third generation light sources, such as the Advanced Light Source (ALS), offer the high brightness that makes high-resolution SXF experiments practical.

Recent SXF experiments have examined the changes in the valence emission spectrum as the excitation energy is varied. A valence emission spectrum results from transitions from valence band states to the core hole produced by the incident photons. In the nonresonant energy regime, the excitation energy is far above the core binding energy, and the absorption and emission events are uncoupled. It is similar to valence band spectra in photoemission except for the additional element and angular-momentum selectivity mentioned earlier. In the resonant excitation energy regime, core electrons are excited by photons to unoccupied states just above the Fermi level ($E_F$). The absorption and emission events are coupled, and this coupling may manifest itself in several ways, depending in part on the localization of the core-hole-perturbed empty electronic states in the material. In boron nitride, the valence emission spectrum at resonance is shifted, and reflects the influence of an electron excited to a localized, excitonic state ($\pi^*$ state). The presence of the localized electron (and the core hole) is to screen the valence electrons, resulting in a shift of the valence emission to lower photon energies. Emission is also observed from (normally unoccupied) excitonic (quasibound) states above $E_F$. Resonant SXF experiments involving delocalized final states in graphite, Si, and diamond have found dispersive effects and intensity modulations in the valence emission spectrum as the incident photon energy is varied.

Figure 1 illustrates the use of the resonant SXF technique for probing the structure of different bulk phases of BN. In Fig. 1(a) is shown the boron K fluorescence spectra acquired from probing the structure of different bulk phases of BN. These spectra were obtained using a near-resonant excitation energy of 206 eV. Although the valence band emission region is slightly different for cBN and hBN, by far the most striking difference is the sharp feature at 193 eV from hBN. Similar features arising from emission above $E_F$ have been detected in other resonant SXF work from boron-containing systems such as $\text{B}_2\text{O}_3$. It results from the anomalous inelastic x-ray scattering effect first discovered by Sparks. Its presence in hBN and absence in cBN is easily
understood in light of recent photoabsorption data on these systems. The peak at 193 eV results from resonant emission from an excitonic state which corresponds to a normally unoccupied antibonding state present when boron in these systems is bonded. Hexagonal BN is $sp^2$-bonded, and thus exhibits a $\pi^*$ resonance feature. Since cBN has the diamond structure and is $sp^3$ bonded, there are no empty quasibound states in the region just above $E_F$ from which resonant emission can take place. Thus, the presence of this $\pi^*$ resonance feature is indicative of both the geometric and electronic structure.

Figure 1(b) shows that, in addition to using this feature as a marker for $\pi$-bonded boron, the resonance feature can also be used to detect very small quantities of boron in a material, such as a thin, deeply buried boron-containing thin film. As the incident photon energy is tuned to the resonant energy of 193 eV, the magnitude of the resonance increases dramatically. Its peak intensity is nearly 30,000 times more than the peak valence emission intensity using this excitation energy. The resonant peak's intensity would be even higher were it not for self-absorption effects, which reduce its intensity relative to the valence band emission.

The potential of using resonant SXF for detecting small quantities of $\pi$-bonded boron based on the results above lead us to construct the two buried layer samples shown in Fig. 2. Boron nitride thin films have attractive properties for both tribological coatings and electronic applications. These buried BN layer samples were synthesized by magnetron sputter-depositing 3 Å of BN onto either a clean Si(100) substrate or an amorphous 50-Å-thick carbon buffer layer on Si, that were encapsulated with 50 Å of amorphous carbon. Transmission electron microscopy (TEM) confirmed that the samples possessed the layer structure shown in Fig. 2. The boron present in the samples was undetected by photoemission or photoabsorption. SXF has been used previously to characterize buried Si monolayer films, but only by creating a superlattice of many Si layers and by counting for many hours were statistically significant data acquired. The samples studied here consist of a single 3-Å-thick layer of
BN monolayer present in the C/BN/C sample is much more greater for the C/BN/C system than in the C/BN/Si system. The system studied in this work is inaccessible to traditional surface sensitive techniques, and the element-specific electron structure of a buried thin film is very important to our understanding of these systems. Although we have used resonant SXF to probe the electronic properties of a boron-containing monolayer, the technique should be applicable to other systems with localized antibonding states.

To summarize, we have demonstrated the value of SXF as a nondestructive technique to study the electronic bonding of buried monolayer thin films. The system studied in this work is inaccessible to traditional surface sensitive techniques, and the element-specific electron structure of a buried thin film is very important to our understanding of these systems. Although we have used resonant SXF to probe the electronic properties of a boron-containing monolayer, the technique should be applicable to other systems with localized antibonding states.

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FIG. 3. Resonant fluorescence spectra from the buried monolayer samples shown in Fig. 2, and from a hexagonal boron nitride sample. The $\pi^*$ resonance feature is much more intense in the C/BN/C sample as opposed to the C/BN/Si sample, which indicates that the BN monolayer in C/BN/C is more $\pi$-bonded than in C/BN/Si.