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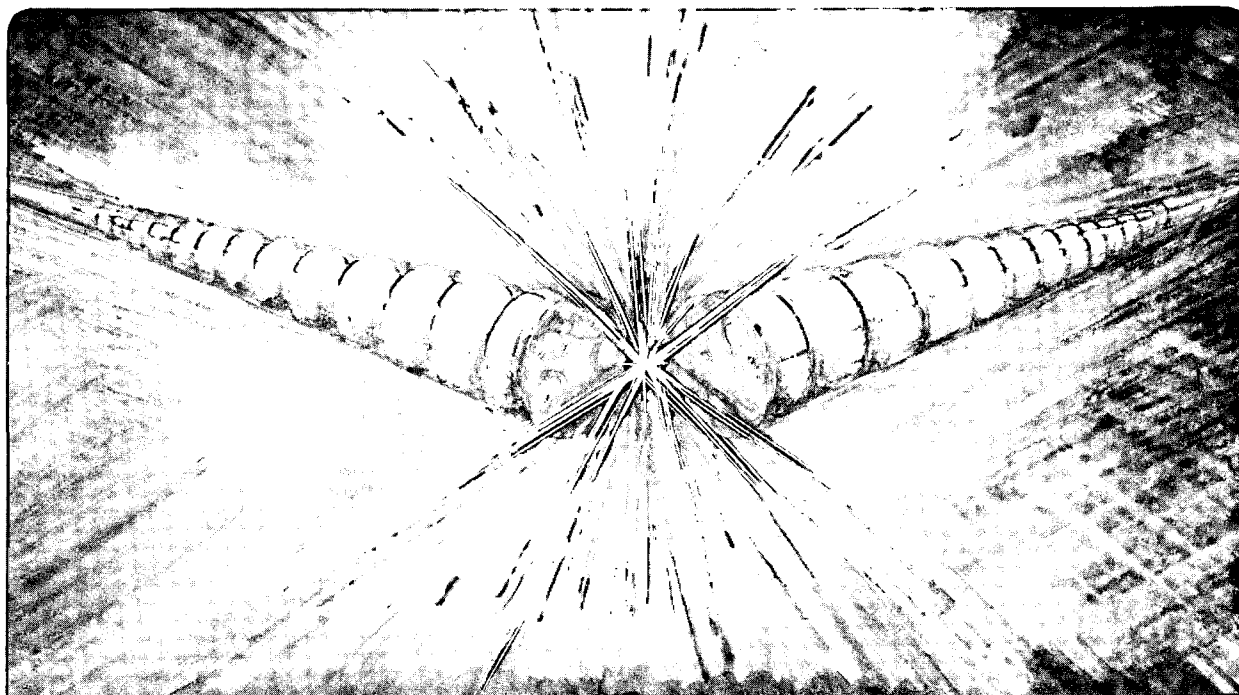
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March 1995



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**CHARACTERIZING BURIED INTERFACES USING
RESONANT SOFT X-RAY FLUORESCENCE***

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Characterizing buried interfaces using 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) with synchrotron radiation. By using the strong π^* resonance feature in the resonant fluorescence spectrum near the B (1s) threshold, we were able to detect the BN monolayer and assay the electronic structure and degree of π bonding at different BN interfaces. Our results demonstrate the capability of the resonant SXF technique for probing the element-specific electronic structure of a buried heterointerface nondestructively.

The atomic-scale properties of interfaces between dissimilar materials have been and will remain a subject of intense investigation [1]. 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 as it exists after many layers are deposited has been questioned in some systems [2]. In this Letter we demonstrate the capability of resonant soft x-ray fluorescence for probing the electronic and geometric structure of buried interface systems which are inaccessible to 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 [3]. Due to the long mean free path of photons in solids (~ 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. In the following we utilize this high brightness to demonstrate the capability of SXF for detecting the electronic structure of monolayer quantities at buried interfaces.

Recent SXF experiments have examined the changes in the valence emission spectrum as the excitation energy is varied [4-8]. A valence emission spectrum results from transitions from valence band states to the core hole produced by the incident photons. In the *non-resonant* energy regime, the excitation energy is far above the core binding energy, and the absorption

and emission events are uncoupled. The fluorescence spectrum resembles emission spectra acquired using energetic electrons, and is insensitive to the incident photon's energy. 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 manifests itself in several ways, depending in part on the localization of the empty electronic state 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 (a π^* state) [4]. 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 [5], Si [6], and Diamond [7], have found dispersive effects and intensity modulations in the valence emission spectrum as the incident photon energy is varied.

Fig. 1 illustrates the use of the resonant SXF technique for probing the structure of different bulk phases of BN. In Fig. 1a is shown the boron K fluorescence spectra acquired from cubic (cBN) and hexagonal (hBN) boron nitride. 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 B_3O_2 [7] and $B_{6,4}Si$ [8]. Its presence in hBN and absence in cBN is easily understood in light of recent photoabsorption data on these systems [9]. The peak at 193 eV results from resonant emission from an excitonic state which corresponds to the (normally unoccupied) π^* anti-bonding state

present when the boron in these systems is π bonded. Hexagonal BN is sp^2 -bonded, and thus exhibits a π^* 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 π^* resonance feature is indicative of both the geometric and electronic structure.

Fig. 1b shows that, in addition to using this feature as a marker for π -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 heterojunction. 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 π -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 [11]. 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. SXF has been used previously to characterize buried Si monolayer films, but only by creating a superlattice of many Si layers, and counting for many hours were statistically significant data acquired [12]. The samples studied here consist of a 3Å layer of BN, and the combination of the very strong resonant feature and the high brightness of the ALS enabled us to detect the buried heterojunction in less than five minutes of data accumulation and to collect

statistically significant spectra in less than thirty. It should be noted that, as synthesized, these samples are inaccessible to electron-based spectroscopies. Although the depth distribution of boron (as well as the other elements present) may be obtained via transmission electron microscopy (TEM) or Rutherford backscattering spectroscopy (RBS), no technique to our knowledge allows the concurrent extraction of element specific *electronic* information (other than macroscopic transport properties such as the Schottky barrier height) from samples such as these.

Resonant and non-resonant SXF spectra acquired from the samples shown in Fig. 2 are shown in Fig. 3. SXF data obtained from a hBN sample under identical conditions are also shown for comparison. The spectra shown in Fig. 3 have been normalized so that the effects of sample position and different incident photon fluxes have been eliminated. As can be seen in Fig. 3, the resonant fluorescence signal from both the C/BN/C and C/BN/Si samples is readily detectable. It is quite clear, however, that the strength of the π^* related signal is much greater for the C/BN/C system than in the C/BN/Si system. This is true both on-resonance as well as off-resonance. This implies that for equal quantities of BN in each sample, the BN monolayer present in the C/BN/C sample is much more π -bonded than the BN in the C/BN/Si sample. Thus, the electronic structure of the buried Boron in each of these systems is significantly different.

It is clear from Fig. 3b that the detection limit for this technique in the present experiment is much less than one monolayer. The peak to background ratio for the C/BN/C interface is ~ 180 , so for this system and apparatus the detection limit is about 0.006 monolayers. In the present experiment a high-resolution (0.3 eV) detector was used, but clearly this is not required to detect the resonant peak. If instead a Ge detector was used, which has a much

higher quantum efficiency and several orders larger detection angle, the detection limit could theoretically be much much lower.

To summarize, we have demonstrated the value of SXF as a non-destructive technique to study the electronic bonding of buried interfaces. The systems studied in this work are inaccessible to traditional surface sensitive techniques, and to our knowledge the element-specific electronic structure of a buried heterointerface has not been realized previously. 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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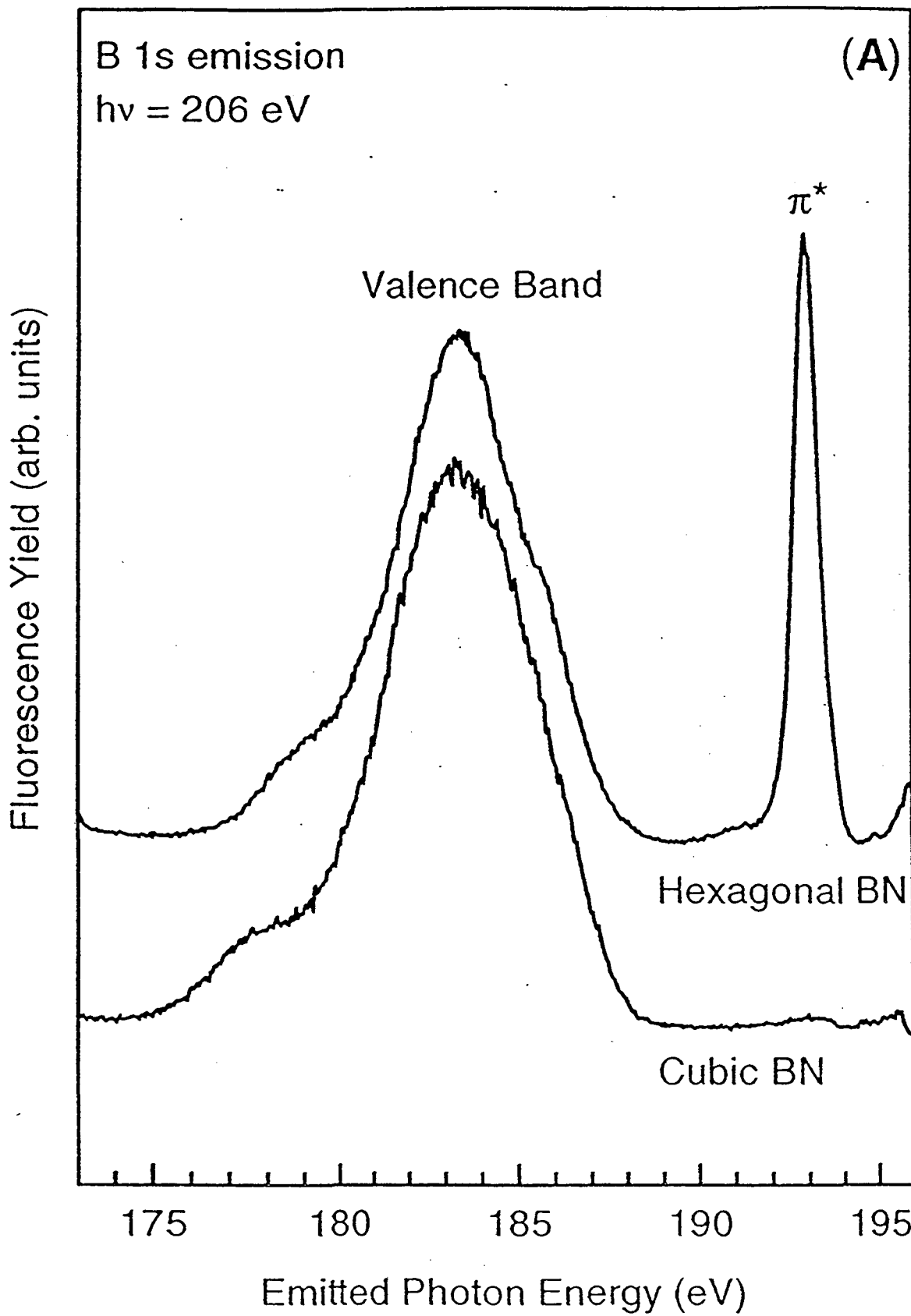
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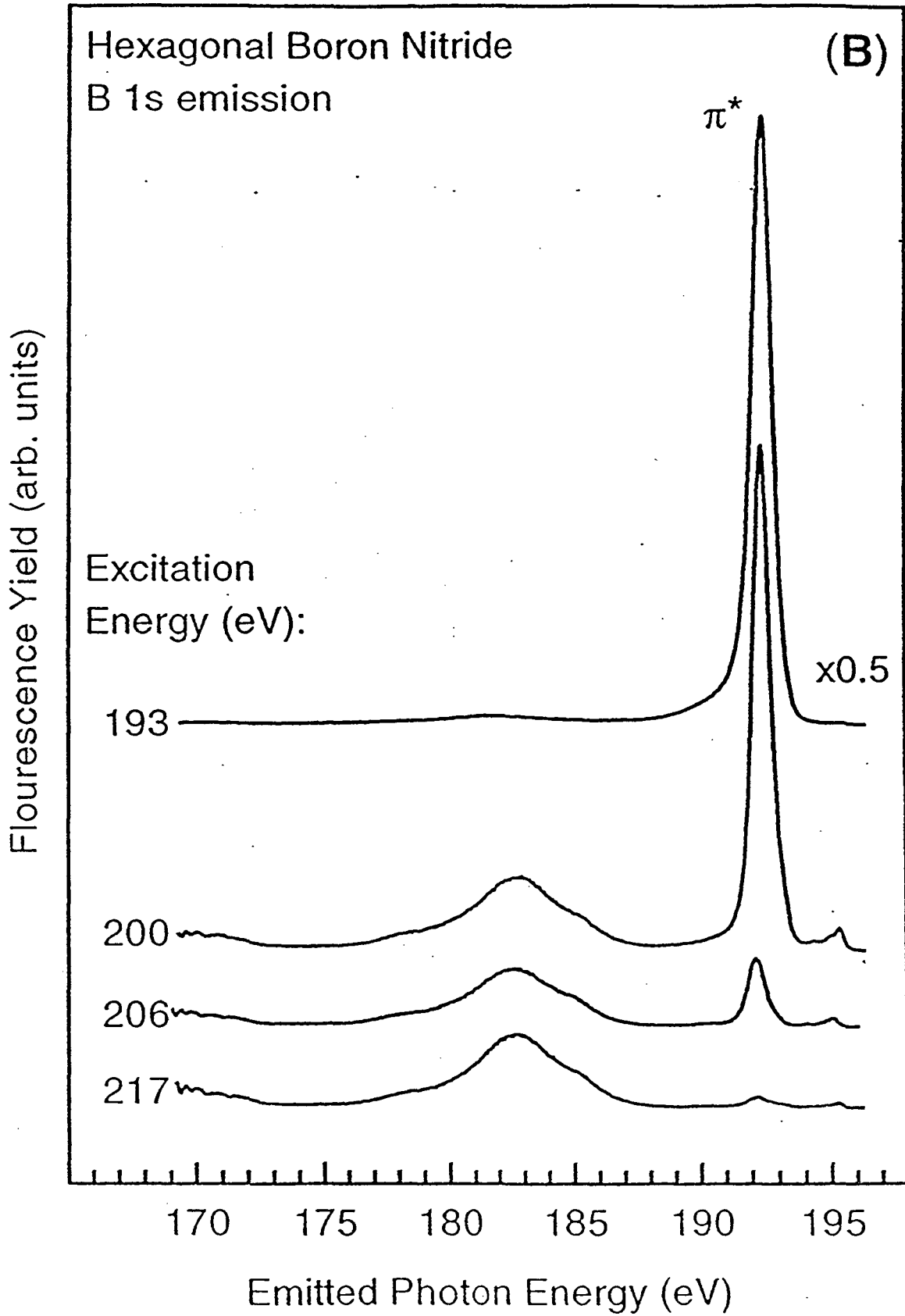
Captions

Fig. 1: (a) Soft x-ray fluorescence spectra measured from hexagonal and cubic BN. Hexagonal BN is π bonded. Emission from quasi-bound π^* states at 193 eV may be viewed in the resonant fluorescence spectrum when in excitation energy is tuned near the π^* resonance energy. Cubic BN is σ bonded (e.g. diamond). There are no empty states near the Fermi level in this system so no emission from quasi-bound states above the Fermi level are detected, as expected. The presence of the quasi-bound feature is thus indicative of the geometric and electronic structure. (b) Resonant fluorescence spectra from hexagonal BN. As the excitation energy is tuned to the π^* resonance, the emission from the quasi-bound state is greatly enhanced.

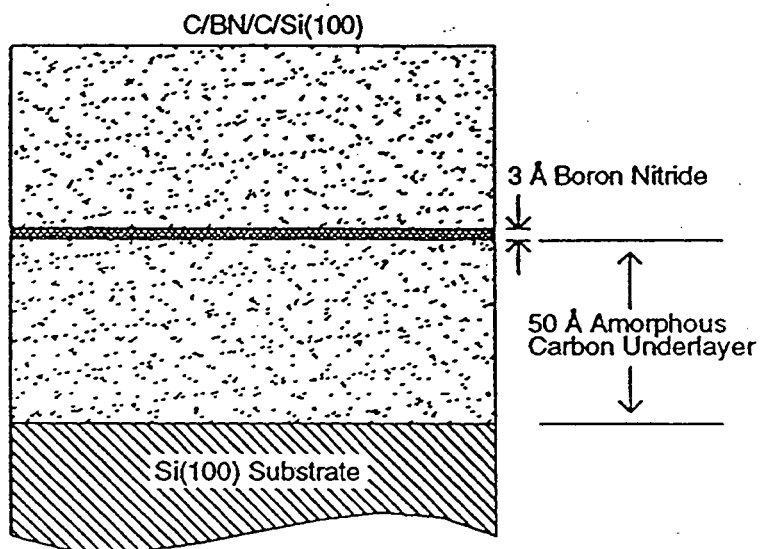
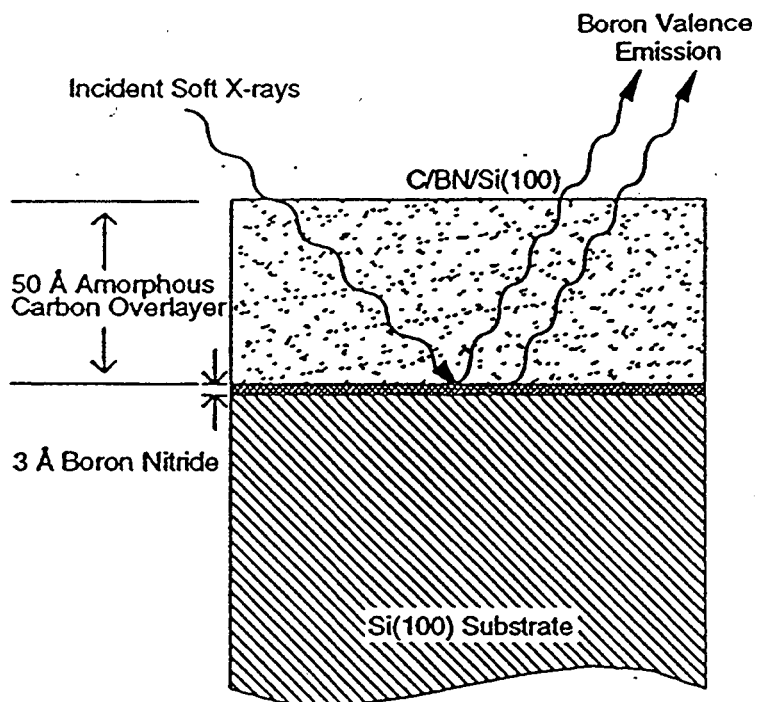
Fig. 2: The buried BN monolayer systems studied in this work

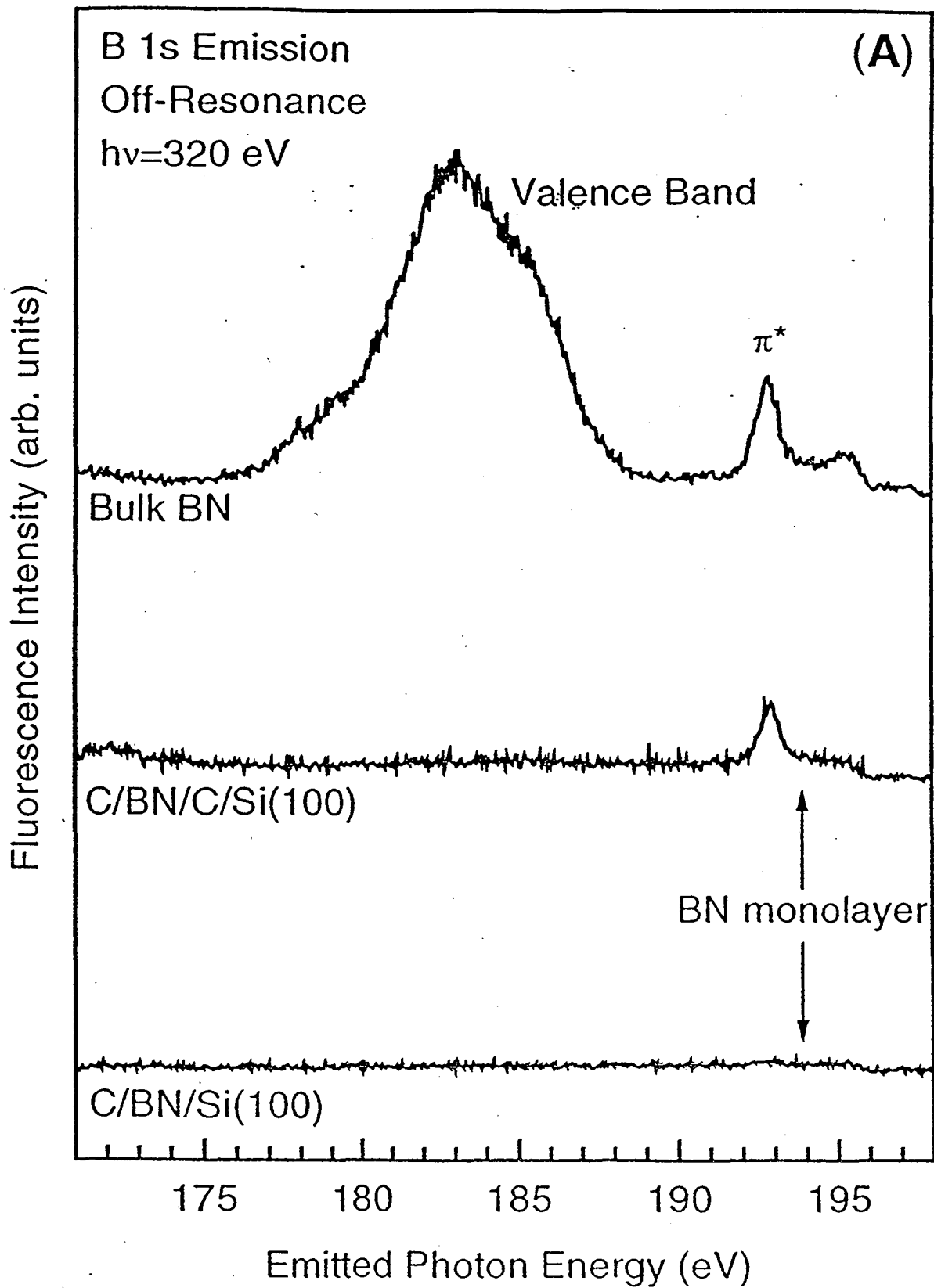
Fig. 3: Resonant (a) and non-resonant (b) fluorescence spectra from the buried monolayer samples shown in Fig. 2, and from a bulk hexagonal sample. The π^* resonance feature is much more intense in the C/BN/C/Si sample as opposed to the C/BN/Si sample, which indicates that the BN monolayer in C/BN/C/Si is more π -bonded than in C/BN/Si. The B valence emission region is magnified in (b) to show the difference in the valence electronic structure between the samples.

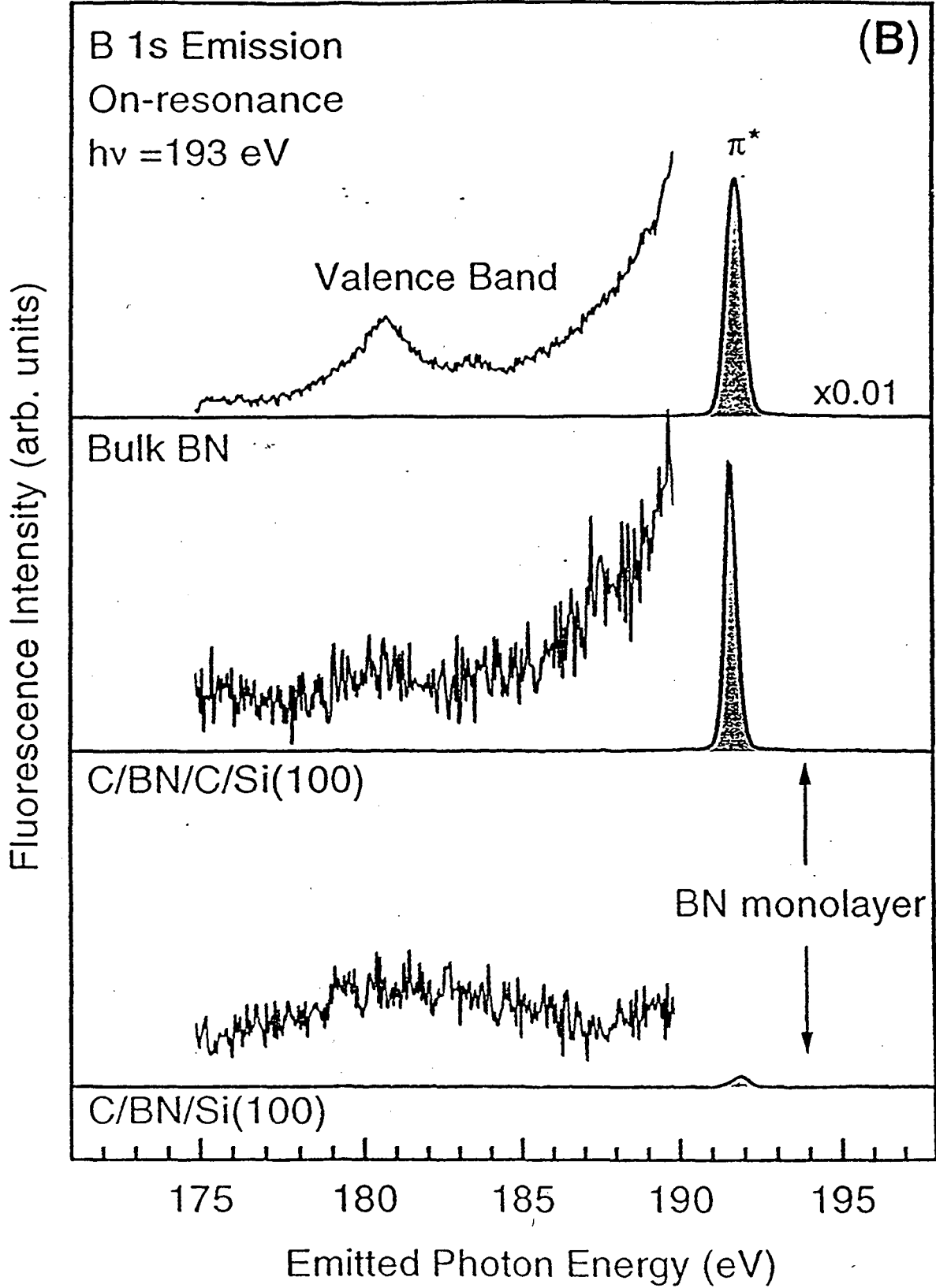




Buried Boron Nitride Monolayer Samples







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