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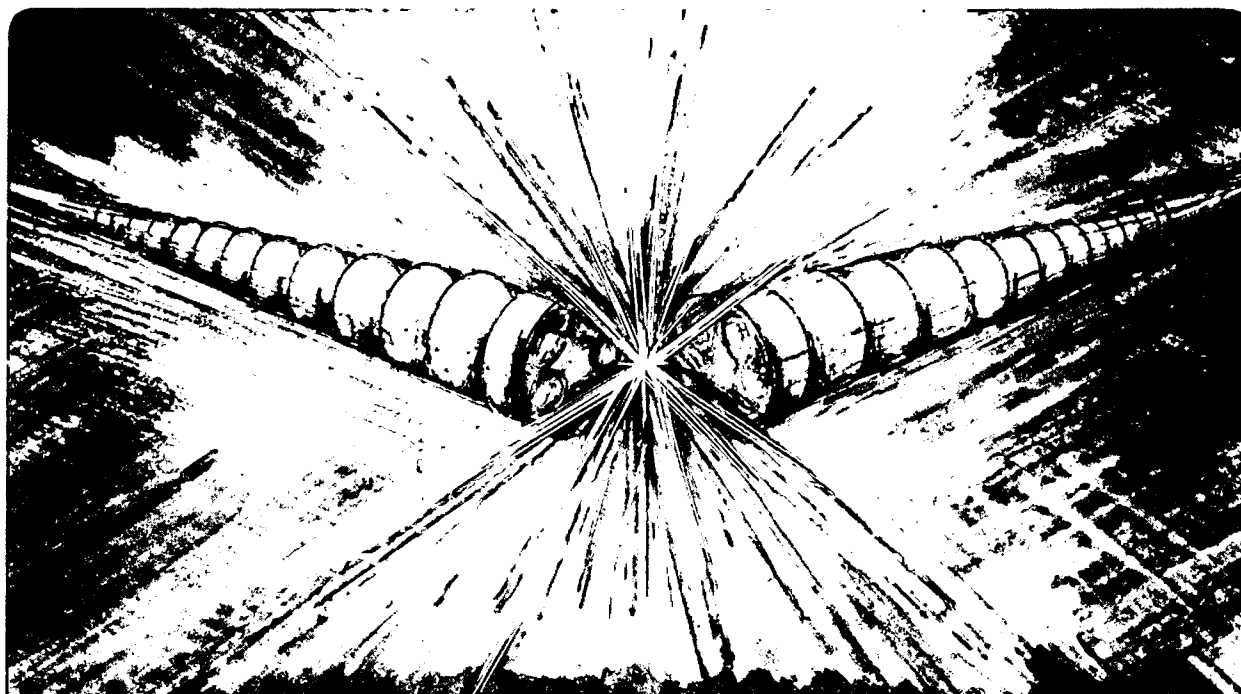# Lawrence Berkeley Laboratory
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Soft X-Ray Fluorescence: A Multifaceted Window to View the Electronic Structure of Matter

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SOFT X-RAY FLUORESCENCE: A MULTIFACETED WINDOW TO VIEW THE ELECTRONIC STRUCTURE OF MATTER

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1. INTRODUCTION

X-rays, as a scientific tool, have been around for a long time [1]. Fluorescence x rays have been detected in the hard x-ray region almost since their discovery [2]. Soft x-ray fluorescence emission is especially powerful because the shallow core levels have a natural width that is about a factor of 10 less than deeply bound levels. Thus, the valence-band spectrum is not unduly broadened by the width of the core level. Furthermore, because the fluorescence photons are not affected by electric and magnetic fields, insulating samples can be studied without experimental complications. Photons produce less damage than other probes and are more bulk-sensitive than electrons. Fluorescence is sensitive to the electronic structure around selected elemental species and thus facilitates the analysis of multicompound samples._ X-ray emission from a specimen also conveys information about the angular-momentum symmetry of the electronic states.

Advancing technology provides new opportunities to make use of the power of photon-in, photon-out methods to study valence electrons in atoms, molecules, and solids. Now that high-brightness synchrotron sources are available, methods for studying the properties of materials by photon-in, photon-out techniques become even more exciting. The fluorescence emission is a very powerful tool to study the near edge x-ray absorption structure in the bulk and from surfaces. Furthermore, multicolor photon experiments using synchrotron light and lasers requiring heroic efforts under present circumstances will become routine at these new sources [3]. Extensive progress has been made in developing multicolor photon experiments to study atomic and molecular processes.

2. INSTRUMENTATION FOR A SOFT X-RAY EXCITATION SCHEME _

Soft x-ray fluorescence is an inefficient process. Its successful use as an experimental tool requires a highly efficient spectrometer coupled with an intense, bright source. Third generation synchrotron radiation sources meet the criterion of brightness and intensity. With high brightness sources, we can achieve higher spectral and spatial resolution. Technical advances that have led to higher resolution have always produced exciting new science. Third generation synchrotron radiation sources like Advanced Light Source (ALS) in Berkeley designed for dedicated experiments by photon users are optimized for high spectral brightness in the soft x-ray and vacuum ultra-violet wavelengths. An insertion device beamline BL 8.0 at ALS is utilizing radiation from a 5.0 cm period undulator

(U5.0) to deliver photons in the 100-1500 eV photon range [4]. The energy resolution, $E/\Delta E$ is better than 10^4 for the 100-200 eV region. Using refocussing optics, over 10^{12} ph/s in a 0.1% bandwidth can be delivered to about 100 μm spot size[5].

One of the five end stations to utilize this undulator radiation is a high resolution soft x-ray emission (SXE) spectrometer, a grazing incidence, Rowland Circle instrument where the diameter of the Rowland Circle can vary from 5 to 10m. This spectrometer, funded by NSF, is designed to match the small phase-space attributes of the high spectral brightness of the beamline optical system. Special features of the SXE spectrometer are four spherical gratings on a carousel mount to cover the energy range of 40-1400 eV and a photon counting area detector. The energy resolution ($E/\Delta E$) of the SXE spectrometer in this energy range is about 1000, sufficient to resolve features in x-ray emission spectra.

A second high efficiency spectrometer [6] is mounted on a beam line at the Center for Advanced Microstructures and Devices (CAMD). It incorporates toroidal gratings which have a gain of 2 to 3 in efficiency over spherical gratings, and a position sensitive detector which further enhances the sensitivity of the instrument by another factor of 100. At CAMD, an electron beam, white light, or monochromatic radiation from the storage ring can be used to excite the sample. With a monochromatized beam, about 10^{13} photons per second fall on the sample in a 0.5 eV band pass with an electron current of 400 mA stored in the ring.

3. PHOTON-IN, PHOTON-OUT RESEARCH OPPORTUNITIES

With traditional e-beam excitation, the structure and energy position of emission spectra in the soft x-ray range are largely unaffected by the excitation conditions. With photon excitation near threshold, however, many recent studies have demonstrated that several distinct physical processes couple excitation and emission. Measurements on molecular gases [7] and crystalline samples of Si and C [8, 9, 10] show a strong modulation of spectral features as a function of photon energy. In systems with localized orbitals, the modulations can be understood as resonant excitation to localized excited states. In Si and C, the effects have been explained as an inelastic process in which crystal momentum is conserved between the excited photoelectron produced by the excitation process and the valence hole remaining after emission.[9] Other near threshold processes include energy shifts produced by excitation into a core exciton states which modifies local

screening[11-14]. and most recently, an inelastic process in which emission is observed at a fixed energy below the excitation energy in a process analogous to the resonant Raman effect. We discuss several of these studies in the following sections.

3.1. THE EXCITATION OF SILICON $L_{2,3}$ EMISSION VS. PHOTON ENERGY

Silicon is a good candidate for the study of band structure because its electronic structure is well known and high quality samples are easy to obtain. In order to confirm the proposed theoretical explanation of threshold effects in Si and C in terms of a k-conserving inelastic process, our group conducted measurements at the NSLS on amorphous and crystalline silicon[10], using a monochromator with a narrow 0.4 eV bandpass. The results are shown in Fig. 1. The amorphous sample shows no dependence of spectral shape on excitation energy, as is expected if the spectral modulation is related to band structure effects that require an ordered structure. On the other hand, emission from the crystalline sample shows a pronounced variation as a function of the excitation energy. Photon excitation energy at 99.7 and 101.2 eV produces transitions to high-density points X and L in the Brillouin zone. Emission from the valence band should be enhanced at these symmetry points, which are indicated by an arrow labeled 1 for the point of X symmetry and 2 for the point of L symmetry. Enhancement in the emission is clearly visible for these symmetry directions. Similarly, other variations in the emission spectrum, such as the changing ratio of peaks A and B, may be explained in the context of this model [10]. The emission spectrum from the valence band gradually resembles the one produced by electron-beam excitation, as the photon excitation energy increases.

3.2. ELECTRON SCREENING AND SPECTATOR DECAY: EMISSION FROM B_2O_3

Our group has observed soft x-ray valence-band emission from a number of insulating compounds, such as MgO and SiO_2. We have studied intermediate coupling [11], temperature effects [12], and phonon relaxation [13] in these compounds. Insulators such as these also have a core exciton as a bound state. In B_2O_3, we have studied the change in the valence emission band as affected by the screening produced by the exciton [14]. Figure 2 is the result of these measurements. Emission spectra from B_2O_3 are shown as a function of excitation energy, indicated by the numbers ranging from 193.7 to 217 eV. The lowest energy of excitation, 193.7 eV, corresponds to that required for the excitation of a core exciton. At this photon excitation energy, one observes resonant fluorescence from the exciton

(omitted for clarity) and emission from the valence band. At resonance with the exciton, emission from the valence band occurs while the exciton acts as a "spectator." At a slightly higher photon energy, off resonance with the exciton, one observes emission from the valence band. The band shifts significantly in energy (almost 2 eV) and changes shape. The shift is due partially to the change in initial- and final-state screening produced by the absence of the electron excited to the bound excitonic state.

The change in shape is possibly due to the inelastic photon-scattering phenomena described in the preceding section, and the large difference in the phonon coupling also contributes to the difference in shape. Off resonance, the valence emission spectrum remains relatively unchanged as a function of the photon energy until hv = 202 eV, when an inelastic collision of the outgoing electron can excite one of the valence electrons into the excitonic state. Then one observes emission from both the exciton and the valence band. The branching ratio for direct excitonic recombination to spectator-valence transitions of the boron K exciton was determined to be 0.28. The large value of the branching ratio suggests that the oscillator strength of the exciton is comparable to the integrated number of electrons in the valence band.

3.3. ELECTRONIC BONDING AT BURIED INTERFACES

Many techniques are available for the study of adsorbates bonded to surfaces, but most of these techniques are not readily applicable to the study of the structure of buried solid-solid interfaces . It is especially important that there is some means to study buried solid-solid interfaces non destructively, because interfaces are common in semiconductor devices and in multilayer coatings. X-ray fluorescence spectroscopy is not surface-sensitive and provides information about the interior of the sample. Furthermore, it is a site-specific technique. We have shown [15] that x-ray fluorescence has potential as a method for the investigation of buried interfaces.

In our earlier study, alternating layers of carbon and silicon were used as the medium to study the interface. Because each layer pair had two interfaces, the signal was amplified by $2N$, where N is the number of layer pairs. If one of the layers was thin enough, the signal was further enhanced because the number of bulk atoms did not overwhelm those from the interface. Furthermore, monochromatic photons were used to excite the sample, and the photon energy was chosen to produce holes in the $L_{2,3}$ shell of silicon but not in the K shell of carbon. Thus, fluorescence radiation from transitions between the valence band and the carbon K hole did not interfere with the intensity distribution of the valence band to $L_{2,3}$ hole transitions

in silicon. In Fig. 3, we show the results for a silicon carbide multilayer. As the layer of silicon relative to that of carbon becomes thinner and thinner it approaches a single layer and the observed fluorescence from the silicon atoms reflects the electronic environment of the silicon atoms at the interface. In our particular case the emission resembled that of amorphous silicon carbide.

We carried this method one step further at the soft x-ray end station at the ALS. A single layer of BN atoms was sputtered onto a silicon substrate and was buried under 50Å of carbon. By tuning the excitation energy to the exciton resonance, resonant fluorescence from BN was obtained, as shown in Fig. 4 .The intensity of the signal from a monolayer suggests that this technique is sensitive to a number of atoms that would be equivalent to substantially less than a monolayer. Also shown in Fig 4.is the B K emission spectrum when the exciting radiation was shifted off resonance. The characteristic of the signal on and off resonance compared to the signal from a bulk sample provide additional information about the electronic environment of the atoms at the interface.

3.4. MOLECULAR GASES

The gas phase x-ray emission spectroscopy using synchrotron radiation has been performed mainly at x-ray energies above 3 keV [16] due to unavailability of strong, large window material, which has an appreciable transmission in the low energy x-ray region (below 1 keV). The high beam brightness of the ALS enable the use of gas cell [17], equipped with a 2500 Å thick Si_3N_4 window for exciting x-rays and fluorescence x-rays. An appreciable signal was observed when the pressure in the gas cell was 1 torr. For the first time, gas phase soft x-ray emission spectra were obtained using synchrotron radiation [18]. The monochromatic radiation from BL 8.0 at ALS was used as the source of excitation. As an example, resonance excited F K emission spectrum of SF_6 (gas) is shown in Fig. 5, where the excitation energy was tuned to the F (1s) -> a_{1g} resonance at 689.0 eV. Changes in F K emission spectral features were observed [18] when the excitation energy was tuned to the various resonance's in F K absorption spectrum of SF_6 and to the continuum.

4. CONCLUDING REMARKS

With the development of intense synchrotron radiation sources based on special insertion devices, the technique of photon-in photon-out soft x-ray spectroscopy has a bright future. This brief summary touched on a some of the recent exciting results that have demonstrated especially the value of photon-in

photon-out soft x-ray spectroscopy as a method to study inelastic x-ray scattering in materials through phonon, photon, and electronic interactions. Fluorescence is sensitive to the electronic structure around selected elemental species and thus facilitates the analysis of multicompound samples. Soft x-ray fluorescence is especially useful because the photons are not affected by electric and magnetic fields, photons produce less damage than other probes, scatter less than electrons and ions, and are more bulk-sensitive than electrons. X-ray emission from a specimen also conveys information about the angular-momentum symmetry of the electronic states.

ACKNOWLEDGMENTS

FIGURE CAPTIONS

Figure 1. Si $L_{2,3}$ soft x-ray emission spectra are plotted for amorphous and crystalline silicon samples with the photon excitation energy as a parameter. The a-Si data are normalized to equal area, while the c-Si data are normalized to the intensity of peak B. The vertical line near peak A of the crystalline data marks the energy position of this peak for higher $h\nu_e$.

Figure 2. Boron K soft x-ray emission spectra from B_2O_3 for different photon excitation energies.

Figure 3. The top two spectra are the $L_{2,3}$ emission from silicon layers 9 Å thick alternating with carbon layers 30 Å thick and from crystalline SiC. The lower two spectra are the $L_{2,3}$ emission from silicon 25 Å thick alternating with carbon and from amorphous silicon. The spectra were excited by a 130-eV monochromatic beam of synchrotron radiation.

Figure 4. Boron K emission spectra from about 3 Å of BN sputtered onto a silicon substrate and buried under 50Å of carbon. By tuning the excitation energy to the exciton resonance, resonant fluorescence was obtained.

Figure 5 Resonance excited F K emission spectrum of SF_6 (gas), where the excitation energy was tuned to the F (1s) -> a_{1g} resonance at 689.0 eV.

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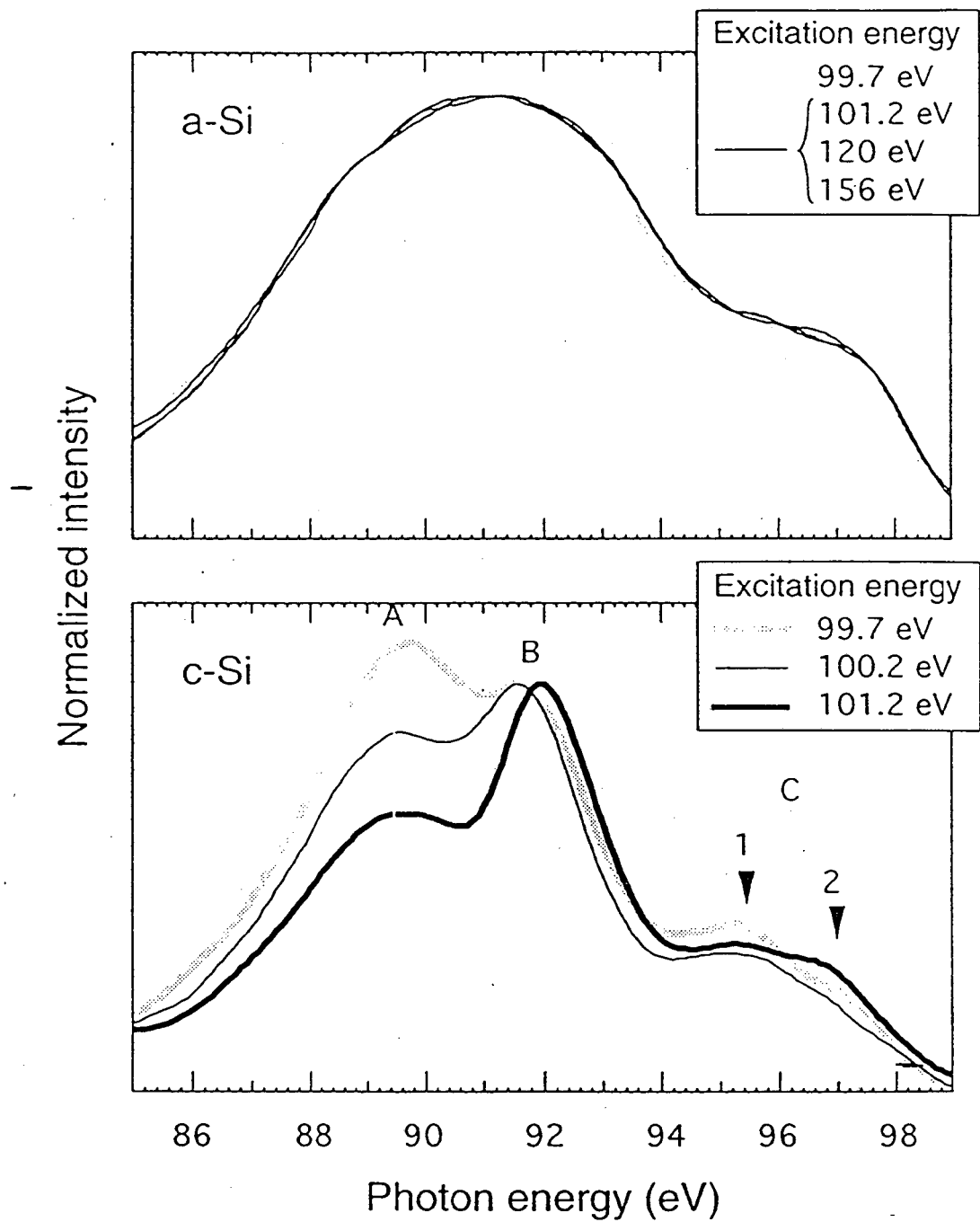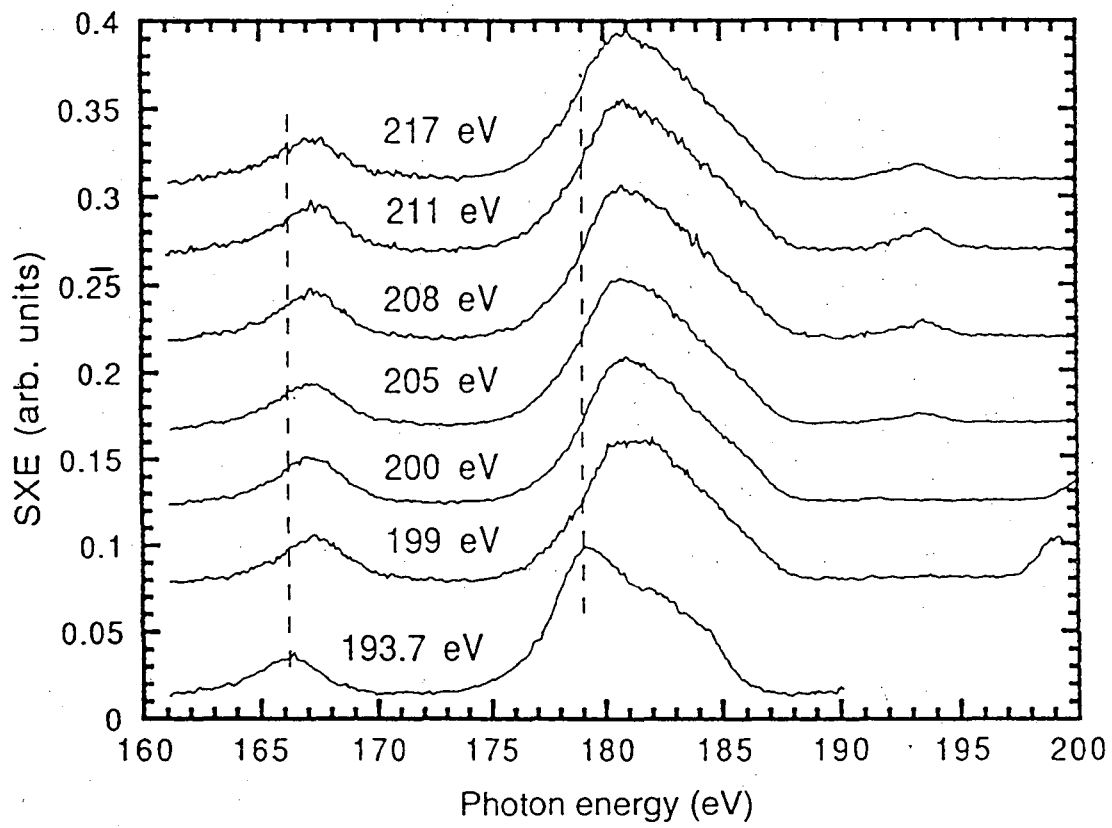
FIGURE 1

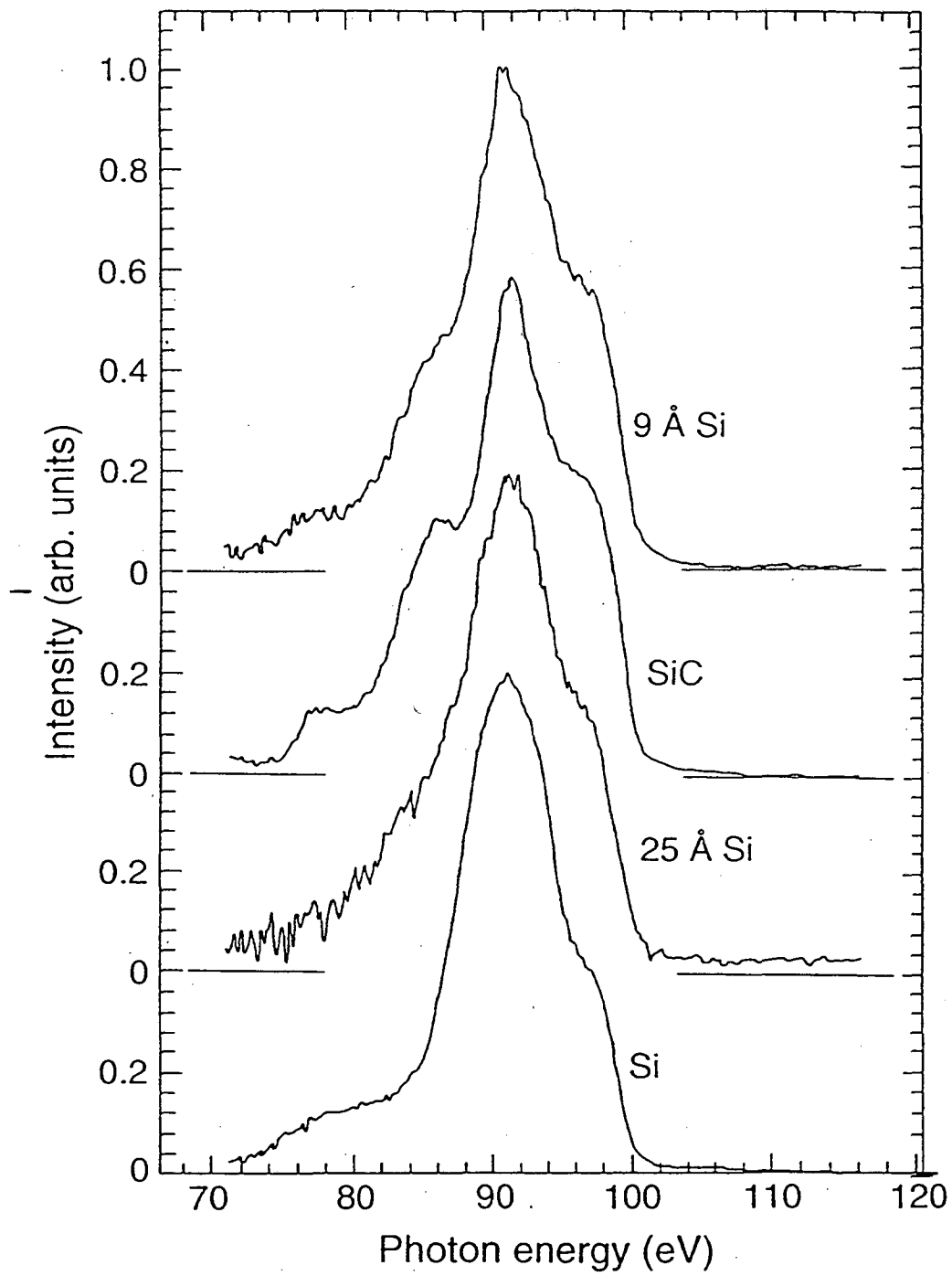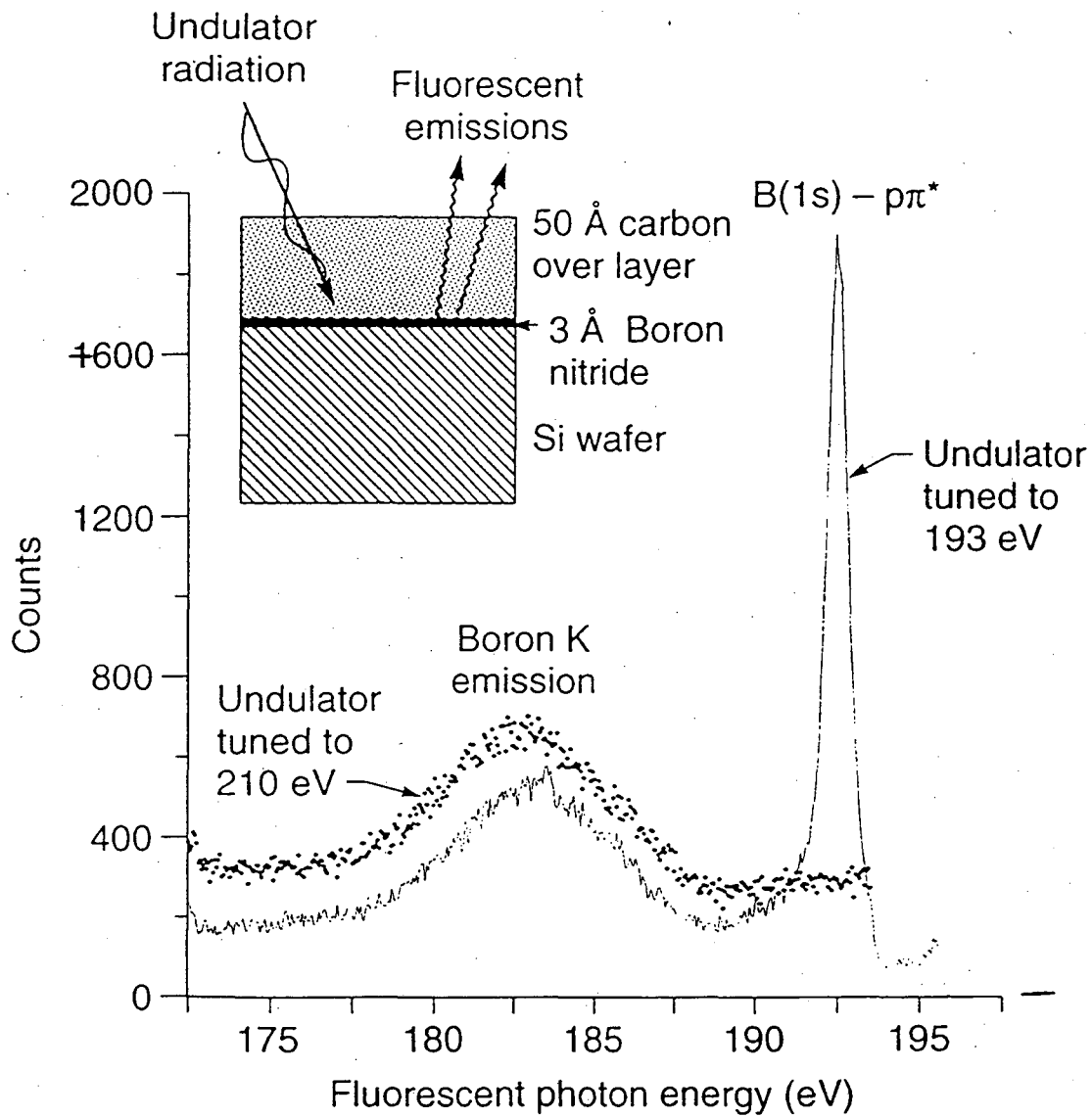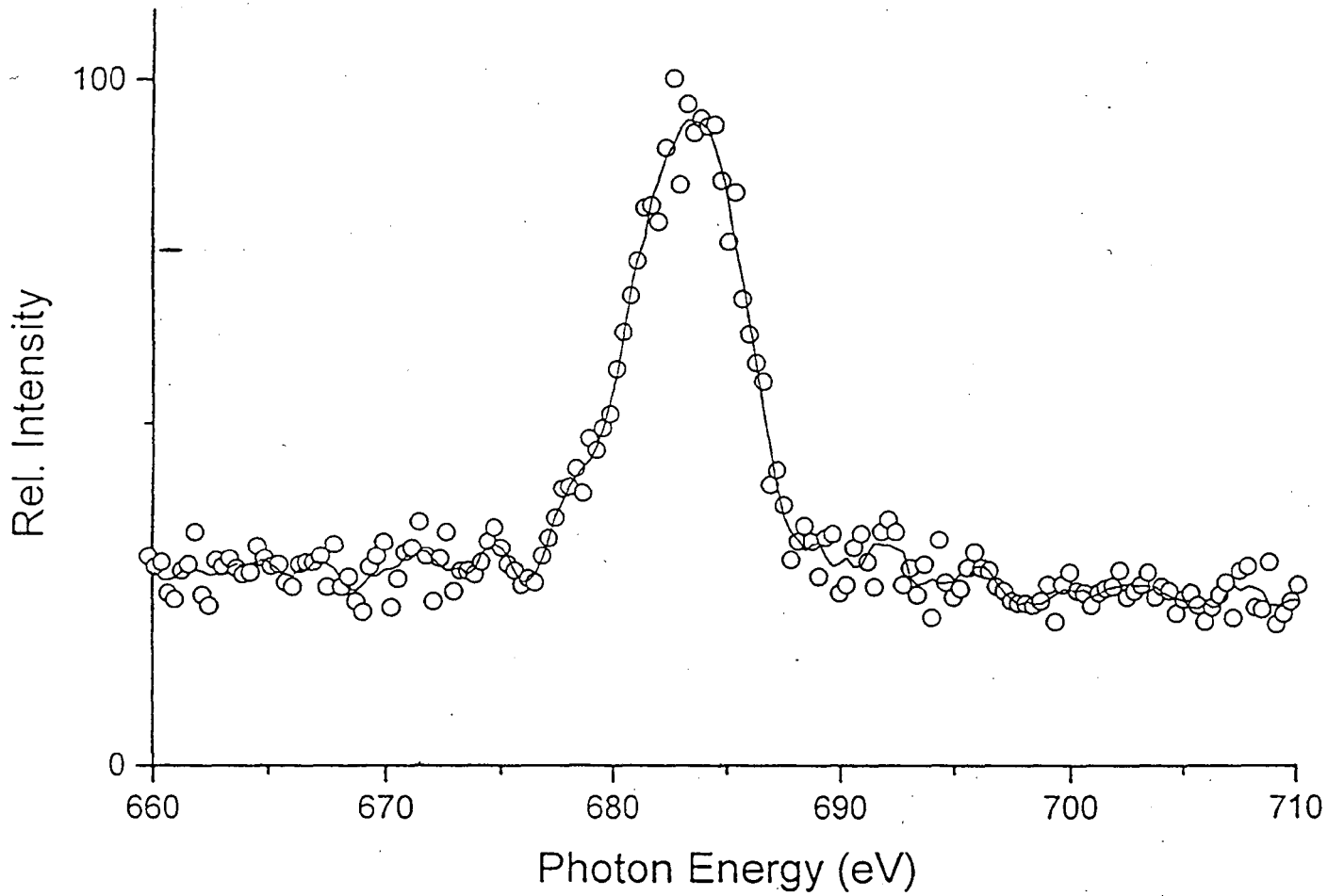**FIGURE 2**

FIGURE 3

FIGURE 4

FIGURE 5

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