# Decay of core excitations in bulk h-BN studied with resonant Auger spectroscopy

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## Abstract

Non-radiative decay of core excitations at the B 1s and N 1s absorption edges of bulk hexagonal boron nitride (h-BN) has been studied with resonant Auger spectroscopy. In order to reproduce the bulk properties of the sample while keeping it electrically conducting, we have grown reasonably thick (more than 20 nm) polycrystalline films of h-BN on a Ni(1 1 1) surface by thermal cracking of borazine vapor. The probability of the participator Auger process in the non-radiative decay of the B $1s^{-1}\pi^*$ and N $1s^{-1}\pi^*$ excitations has been found to be very high (31%) and rather low (below 0.5%), respectively. The drastic difference between the participator Auger decay probabilities of these two excitations has been explained in terms of different localization of the electrons promoted into the lowest unoccupied $\pi^*$ state on the cationic (B) and anionic (N) sites.
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## 1. Introduction

Hexagonal boron nitride (h-BN) is a well known insulating and chemically inert compound isoelectronic and structurally similar to graphite. Due to its layered structure it exhibits a variety of essentially two-dimensional properties, including the recently discovered ability to form nanotubes [1,2]. The formation of the B 1s and N 1s core-excited and core-ionized states in h-BN has been extensively studied by soft X-ray absorption (XA) [3–10], electron energy loss spectroscopy [11–12] and X-ray Raman spectroscopy [13]. The radiative decay of the B 1s core excitations was investigated using resonant x-ray emission spectroscopy by O'Brien et al. [14], while the non-radiative channels were studied with resonant Auger spectroscopy by Barth et al. [4] and by Shimada et al. [15]. The most drastic effects were observed in both cases in the decay of the B $1s^{-1}\pi^*$ excitation corresponding to

the first $\pi^*$ resonance in the B 1s near-edge X-ray absorption fine structure (NEXAFS). In particular, the probabilities for the participator decay processes (i.e., processes with a direct participation of the electron promoted into the lowest $\pi^*$ orbital, also called direct recombination) were estimated to be as large as $(8 \pm 3)\%$ for the radiative channel [14] and 33% [4] or $(66 \pm 8)\%$ [15] for the non-radiative channel. The latter values are surprisingly high even for atomic and molecular species, while for solids, where normal Auger decay resulting from the electron hopping may additionally shorten the lifetime of a core excitation, they are extraordinary high.

In order to clarify the situation with the direct recombination probabilities in the non-radiative decay of core excitations in h-BN we decided to re-investigate the resonant Auger spectra at the B 1s absorption edge and to complement these data with the decay spectra at the N 1s edge. Our goal is to obtain more reliable values for the participator Auger rates by means of a considerable improvement of the spectral resolution and a more efficient suppression of the sample charging in comparison with the earlier studies [4,15].

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## 2. Experiment

The experiments were performed at the soft X-ray beamline D1011 of the MAX-II storage ring (MAX-lab, Lund, Sweden), equipped with a modified SX-700 plane-grating monochromator. The photon energy resolution was set to 50 meV at the B K-edge (~190 eV) and to 150 meV at the N K-edge (~400 eV). The end station is equipped with a high-resolution SES-200 electron energy analyzer, LEED optics, an ion gun for the substrate cleaning, a gas-sending system and a multi-channel plate electron yield detector. The kinetic energy resolution was set to 75 meV for all electron spectra. All B 1s and N 1s NEXAFS spectra were measured in the partial electron yield mode with a repulsive potential of −100 V. The incident beam intensity was recorded simultaneously with the XA spectra by a gold mesh monitor. All measurements were carried out under ultra-high vacuum conditions, at a base pressure below $1 \times 10^{-10}$ mbar.

Boron nitride was grown in situ by the thermal cracking of vaporized borazine (from Boron Biologicals, Inc.) at the Ni(1 1 1) surface, which was pre-cleaned by several cycles of Ar$^+$ sputtering ($U = 1$ kV) and annealing ($T = 800$ °C, measured by a thermocouple directly attached to the crystal). A sharp hexagonal (1 x 1) LEED pattern was characteristic for the clean substrate, and no traces of surface contaminations could be detected on it by X-ray photoemission spectroscopy (XPS). The substrate was maintained at 800 °C during the borazine decomposition. The vapor exposures were measured with a standard ion gauge located about 20 cm away from the borazine dozer, without any correction for the vapor pressure gradient between the dozer and the gauge. Relatively low exposures (about 100 L) resulted in the epitaxial growth of exactly one monolayer h-BN on Ni(1 1 1) [16], while at least $1 \times 10^5$ L was necessary to produce a reasonably thick film. The spectra presented in this paper are recorded from a film, which was at least 20 nm thick, since no signals from the substrate could be detected neither with XPS nor with the total electron yield. On the other hand, the film was thin enough to considerably suppress sample charging. Although no LEED pattern could be detected from this sample, the h-BN film was not completely disordered, as can be concluded from the angle dependence of the B 1s and N 1s NEXAFS. Probably the single h-BN crystallites were too small and disoriented to provide any LEED pattern. The concentration of point defects in the h-BN film was below a detectable limit, since we did not observe in the B 1s and N 1s NEXAFS any features characteristic for vacancies and other imperfections [17].

## 3. Results and discussion

Typical B 1s and N 1s NEXAFS recorded from our h-BN film with the angle $\Theta = 50°$ between the surface normal and the direction of photon polarization are presented in Fig. 1. They are aligned using the difference of 207.67 eV in binding energies of the boron and nitrogen 1s electrons as measured
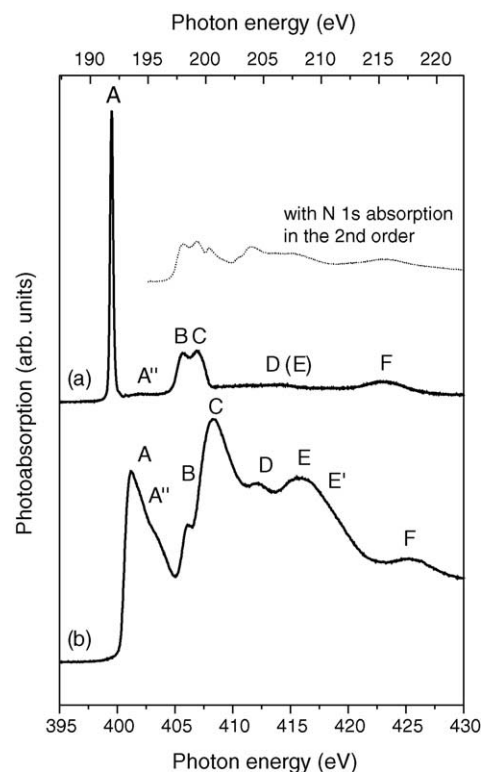


Fig. 1. B 1s (a) and N 1s (b) NEXAFS in the h-BN polycrystalline film. The B 1s spectrum is cleaned from the N 1s contribution in the second-order light. The original spectrum is shown by a dotted line. B 1s and N 1s spectra are aligned in energy using the measured difference of 207.67 eV in binding energies of the boron and nitrogen 1s electrons.

with XPS. In the original B 1s spectrum a strong contribution of the N 1s absorption in the second-order light has been detected (dotted curve in Fig. 1), which was carefully subtracted after a proper fit of the N 1s spectrum in the B 1s curve.

Our NEXAFS spectra of the in situ grown h-BN sample are similar in major details to those measured in the earlier works for ex situ prepared (mainly powders) [3,6–10,15] and in situ cleaved [4] samples. Feature A, which is lowest in energy, is due to the occupation of the lowest antibonding π* states of h-BN. In the B 1s spectrum peak A is much narrower, and its energy is 1.65 eV lower than in the N 1s spectrum as a consequence of a stronger localization of the core excitation on the cationic site. The position of peak A in the B 1s NEXAFS is below the conduction band minimum [3], which led to the description of this feature as a core exciton with a binding energy of 1.9 eV [5] or 1.7 eV [18]. Although the term "core exciton" is widely used in the literature for the description of peak A in the B 1s NEXAFS of h-BN, it seems to be somewhat misleading in this case, because it implies that the corresponding state is absent in the density of states undisturbed by a core hole. On the other hand, a molecular orbital (MO) description of the low-lying 1s NEXAFS features in h-BN can be very instructive. Indeed, one can find striking similarity between the B 1s NEXAFS in h-BN and the free BF$_3$ molecule [19], which is isoelec-