ESRF	**Experiment title:** **X-ray diffraction studies on stress-released cubic boron nitride thin films**	**Experiment number:** **ME-706**
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Report

The aim of this work was to investigate the mechanisms of ion-induced stress relaxation in magnetron sputtered cubic boron nitride (cBN) films. The stress relaxation was achieved by simultaneous medium energy (2-10 keV) Ar/N_2 ion bombardment during the growth process[1]. The relaxation process was verified by measuring *in-situ* the level of macroscopic stress (substrate curvature method) during growth. The purpose of x-ray diffraction (XRD) measurements was to study the stress relaxation at a microscopic scale and discern the mechanisms involved in the process.

a) Experiment:

A set of samples with different degree of ion induced damage, as quantified by the number of displacements per atom (dpa), were prepared at the home laboratory. A sample grown without medium-energy ion bombardment was used as a reference for cBN with high compressive stress (-9 GPa). The macroscopic stress decreases with the number of dpa and ranges from -2.5 to -1.6 GPa for the samples measured at the ESRF (between 0.6 and 1.2 dpa).

Grazing incidence diffraction (GID) geometry was chosen to minimize the signal coming from the single crystal Si(100) substrate. The wavelength of the incidence x-ray beam was set at 1.2 Å (10.332 keV) and the angle of incidence (θ) at 0.2°, slightly above the critical angle (α_c=0.19°) to enhance the scattered x-rays intensity. For each sample, in-plane (2ω) and out-of-plane (2θ) scans were performed, which allows to map the state of biaxial stress in the films.

b) Results:

Figure 1 shows the in-plane (a) and out-of-plane (b) diffraction patterns. In the in-plane geometry, the Bragg peaks related to the hBN(002) and cBN(111) reflections are observed. The hBN signal comes mainly from the seed layer necessary for nucleation of cBN. The hBN(002) peak vanishes in the out-of-plane geometry due to the preferential orientation of this buffer layer with the c-axis parallel to the substrate. A preferential (111) in-plane texture of the cBN grains is observed for the non-irradiated sample. This texture decreases with the introduction of medium-energy ion bombardment.

Figure 2 shows the lattice parameters obtained from Figure 1. For comparison, the d(111) tabulated value of polycrystalline cBN[2] is also included (dashed line). The lattice parameter is larger in the out-of-plane than in in-plane direction, indicating a pronounced biaxial state of compressive stress. Even with the presence of compressive stress, the in-plane d(111) values of our samples are larger than the powder reference value. This is most likely due to the nanocrystalline structure and incorporation of defects as a result of the deposition process. The cBN grains are elongated parallel to the film surface, with a size of ~3 nm out-of-plane and 6 nm in-plane. Despite the ion-bombardment, the FWHM of the Bragg peaks remains the same for all the samples studied, indicating no amorphisation of the cBN phase.

In the case of post-annealing at 900°C of a sample with 1.2 dpa (performed at the home laboratory), the analysis shows a complete relaxation of the lattice with equal in-plane and out-of-plane lattice parameters. The obtained d(111) value can be considered as a reference for stress-free cBN films produced by magnetron sputtering. In the case of medium-energy

ion bombardment, the in-plane and out-of-plane lattice parameters approach the value of the annealed sample with increasing the ion induced damage as a signature of the stress relaxation.

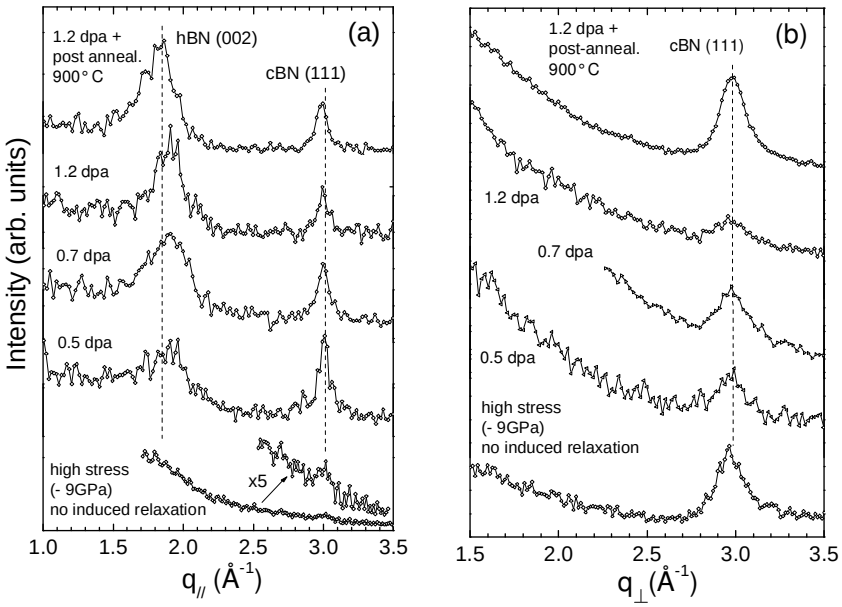

Figure 1. In-plane (a) and out-of-plane (b) diffraction pattern of cBN thin films with different stress relaxation as result of the growth under different induced damage by Ar/N_2 medium-energy ions. The in-plane spectrum of the non released sample shows a very low intensity due to the extreme small film thickness of only 30 nm.

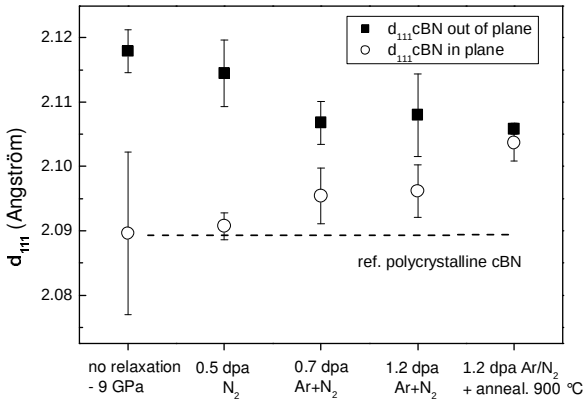

Figure 2. cBN (111) lattice spacing measured in in-plane and out-of-plane geometry for samples with different degree of ion-induced damage and stress relaxation. For comparison the values of polycrystalline cBN, a non relaxed cBN thin film and a cBN thin film that is stress free after annealing at 900°C are shown.

c) Final remarks and out-look:

XRD measurements with a lab-source (Cu-Kα, λ=1.54 Å) were not successful due to the low scattering cross-section of B and N, the nanocrystallinity of the samples and the low film thickness (< 0.5 μm). In view of the above results, the use of synchrotron radiation is clearly justified. However, even when using synchrotron radiation, the set-up has to be chosen carefully (scattering from air,…) to detect such a weak signal.

In conclusion, it can be stated that the observed ion-induced stress relaxation takes place at a microscopic scale. The main path is strain release in the cBN grains and not phase transformation to hBN. In addition, the cBN grains are stable against the ion bombardment, since no signs of amorphisation could be detected.

For future measurements, it would be interesting to performed in-depth studies due to the layered structure of the films. We might also gain some additional information with *in-situ* annealing experiments. Finally, the use of an ID beamline or, at least, operation mode with "Uniform Filling" mode is suggested to compensate the large acquisition time required for this kind of films.

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REFERENCES:

[1] Abendroth et al. Thin Solid Films 447-448 (2004) 131; [2] JCPDS pattern 25-1033.