

CHARACTERIZATION OF TRACE Ni IN A SYNTHETIC DIAMOND BY SYNCHROTRON RADIATION X-RAY FLUORESCENCE ANALYSIS

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A combination of synchrotron radiation (SR) excitation and x-ray fluorescence (XRF) detection has realized analytical microscopy with trace sensitivity. Employing the SRXRF technique, single diamond crystals were investigated which were grown in a Ni based metal solvent with high temperature and high pressure. XRF imaging has visualized the Ni distribution in the sample, and the concentration of Ni was determined with a novel quantification method. Furthermore, small area x-ray absorption fine structure (XAFS) measurements have been carried out, and it was confirmed that the dissolved Ni atoms have a different chemical state from those in metallic state.

1. INTRODUCTION

Trace sensitivity of synchrotron radiation (SR) x-ray fluorescence (XRF) analysis has been widely recognized after Sparks examined the existence of an ultra heavy element with SRXRF¹⁾. Advantages of SR excitation such as trace sensitivity, small background and energy tunability are due to its characteristics; high brilliance, linear polarization and continuum energy distribution.

To realize spatial resolution without losing photon flux, a Pt coated ellipsoidal mirror has been designed and developed which converges the source divergence into a focused spot of approximately 200 μm in diameter. As the intensity gain is more than one hundred, small area x-ray absorption fine structure (XAFS) measurements were first realized²⁾ with this system.

Utilizing this system, trace impurities in synthetic diamonds have been investigated. Among several kinds of metals, only Ni can be dissolved into the diamond lattice. Moreover, Ni XRF imaging of the diamonds clearly demonstrated dissolved Ni exists selectively in the {111} growth sectors³⁾. The

current interests are on the relation between the solvent composition and Ni concentration, and on the chemical state of dissolved Ni.

2. EXPERIMENTAL

2.1 Small area SRXRF system

Experiments were carried out at the Photon Factory in Tsukuba on the Beamline (BL) 4A. Figure 1 shows a small area SRXRF system which was described previously⁴⁾. To minimize background caused by the scattered x-rays, a Si(Li) detector was placed in the electron orbit plane of the storage ring and its direction was normal to the incident beam. Intensities of both incident and transmitted x-rays were monitored with ionization chambers. Samples can be scanned in the x and y directions and XRF images were obtained by collecting XRF signals at each position on the sample. The incident beam energy can be selected by the monochromator in the BL-4A, and XAFS measurements of trace elements can be realized by employing the fluorescence detection method.

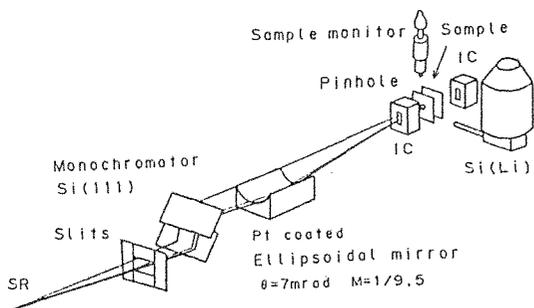


Figure 1. A schematic layout for small area SRXRF analysis⁴⁾ at the Photon Factory.

2.2 Sample preparation

Two synthetic diamond crystals were examined. One was grown in Ni-Fe alloy solvent (sample A) and another was grown in a Ni based metal solvent with additional Ti as a nitrogen getter (sample B). Samples A and B were polished into plates of thickness 277 μm and 258 μm , respectively. With these samples, the spatial resolution was determined by the sample thickness. Each sample was fixed onto a plastic sheet to reduce inelastic scattering which overlaps with the XRF signals. The Ni and Fe concentrations in the plastic sheet were less than the detectable limit.

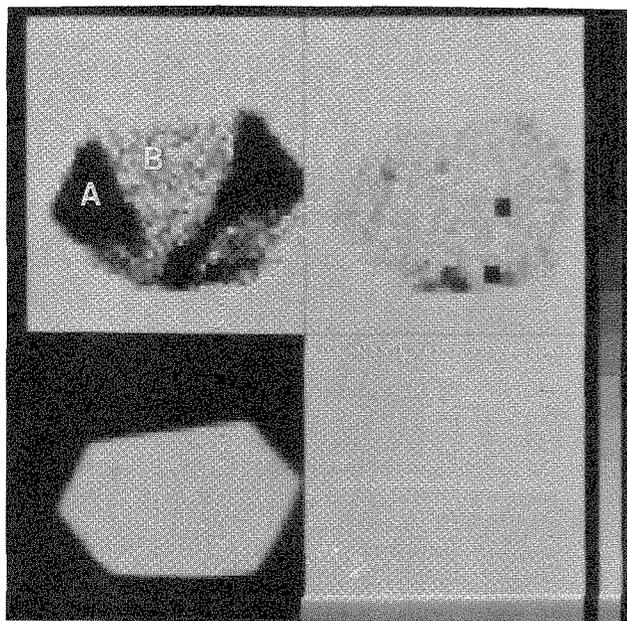


Figure 2. X-ray images of the sample A. (upper left) Ni K-L, (upper right) Fe K-L and (lower left) transmitted x-rays. The scanned area was 4 mm square.

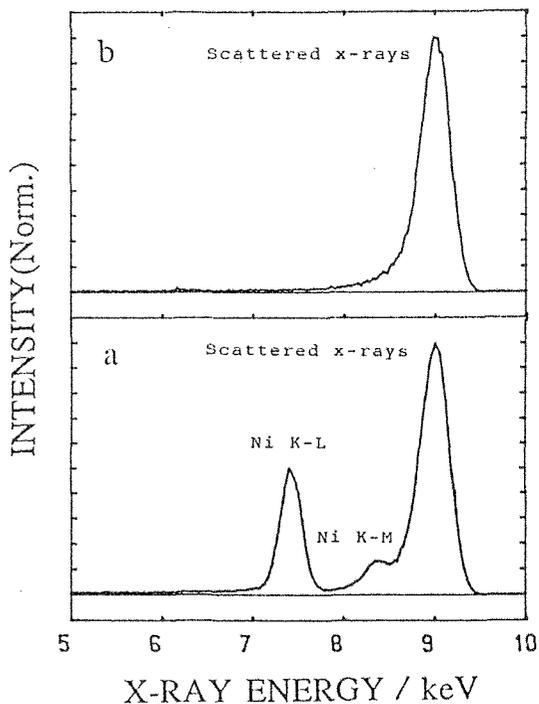


Figure 3. SRXRF spectra from a sample A. a) {111} growth sector and b) {100} growth sector.

3. X-RAY IMAGING RESULTS

Figure 2 shows x-ray images of the sample⁵). Black regions indicate strong signals. The incident x-ray beam energy was selected to be 9 keV to optimize the sensitivity for Ni. As previously reported with this sample³), the Ni image clearly shows a difference between the {111} and the {100} growth sectors. There are several regions in the Fe image which give strong signals. These areas may be attributed to inclusions because both Fe and Ni give strong signals and because a reliable Fe signal was only detected in these regions. Figure 3 shows SRXRF spectra obtained at positions marked on figure 2. The minimum detection limit of Ni for 1000 s data acquisition was 30 ng/cm² which corresponds to 0.3 ppm in concentration.

4. QUANTIFICATION METHOD

To determine the dissolved Ni concentration, a series of reference samples is usually required because the XRF intensity is strongly affected by sample thickness. To overcome this problem, a novel quantification method⁶) was invented. When monochromatic x-rays are used as an excitation beam and when their energy is optimized for an element of interest, XRF signals I_f from the element of interest can be theoretically described.

$$I_f = k I_0(E) W_i \rho t F \quad (1)$$

$$\text{with } F = \{1 - \exp(-At)\} / At \quad (2)$$

$$\text{and } A = \mu(E) / \sin\phi + \mu(E_f) / \sin\psi \quad (3)$$

where $I_0(E)$ is the intensity of the incident x-rays, ϕ and ψ are the glancing angle and takeoff angle, μ is the linear absorption coefficient, E and E_f are the energies of the incident x-rays and fluorescent x-rays, W_i is the weight fraction of the element of interest, t is the sample thickness, ρ is the

sample density and k is a constant.

The absorption correction coefficient F in Eq.(2) represents the attenuation of both incident and fluorescent x-rays in the sample. Therefore the corrected XRF intensity I_f/F becomes proportional to the surface density of the element of interest $W_i \rho t$, and quantification can be performed by comparing the XRF intensity with that of a reference sample of given surface density.

Utilizing the energy tunability of SR, F can be easily determined by the transmittance measurements with energy E and E_f . As $\mu(E)$ is well known for diamonds, a transmittance measurement provides accurate sample thickness. Therefore W_i can be derived. The advantage of this quantification method is that a single reference sample is enough for the quantification and it can be commonly used for other samples.

As a result of quantification, the dissolved Ni concentration was found to be 30 ppm for sample A. In the case of sample B, a typical position was investigated after the XRF imaging. The resultant Ni concentration was 165 ppm. An evaporated Ni film of thickness 344 Å was used as a reference sample. A large concentration difference between two samples is now under considerations.

5. Ni XANES MEASUREMENT

To investigate the chemical state of dissolved Ni, x-ray absorption near edge structure (XANES) measurements were carried out at the same positions where the Ni concentration were determined. Figure 4 shows that dissolved Ni gives a characteristic XANES which is completely different from metallic Ni. Therefore it is confirmed that Ni atoms in the diamond are not due to small inclusions but are dissolved into the diamond lattice. From consideration of the pre-edge peak in XANES, Ni seems to

be in a tetrahedral site according to an empirical rule. For further discussion, theoretical calculation and other spectroscopic information are necessary.

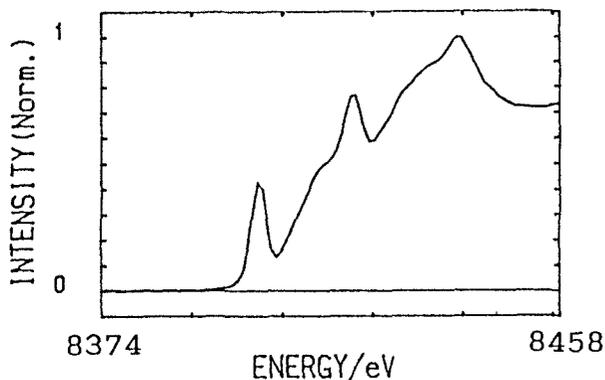


Figure 4. Ni XANES obtained in the small region in the sample B where the Ni concentration is 165 ppm.

6. CONCLUSION

A small area SRXRF system has enabled both trace element analysis from XRF spectra and chemical state analysis from XANES while maintaining spatial resolution. Selective dissolution of Ni into {111} growth sectors was confirmed by Ni XRF imaging. A novel quantification method and small area XANES technique provide quantitative and chemical state information of dissolved Ni in the diamond lattice.

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