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The displacement disorder of atoms in diamond crystals revealed by X-ray imaging plate detector

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ABSTRACT

Cylindrical Imaging Plate Area Detector of Rigaku (IPD) was used to register the X-ray diffraction patterns from diamond crystals grown by Chemical Vapor Deposition (CVD) process. The analysis revealed a deviation from cubic diamond lattice symmetry. X-ray diffraction patterns have been taken by oscillation and stationary crystal methods. Due to high resolution, sensitivity and speed, the IPD detector, allows registration of scattering in the vicinity of Bragg reflections such as broadening, splitting, and satellite reflections. These details were recognized via comparison with the diffraction pattern from a nearly perfect natural diamond crystal and a single crystal of silicon, which were used as diffraction standards. We report data on highly oriented diamond film (HOD) on (001) Si. Powder diffraction patterns show a split of the 111 diffraction line. The line at 2.056 Å corresponds to cubic diamond, and the other line at 2.036 Å is assigned to a disordered polytype. Two superstructure spots were located at 4.076 Å and 4.092 Å. Creation of this polytype during growth annihilates desired heteroepitaxy. The issues of lattice disorder, specifically for diamond crystals, are discussed in the framework of kinematical theory of X-ray diffraction.

1. Introduction

This paper reports X-ray diffraction data for natural diamond and CVD diamond crystals. The deposition of highly oriented diamond (HOD) on (001) silicon substrate represents highly disordered material. Earlier studies were focused on achieving heteroepitaxy of diamond on Si for fabrication of electronic devices. However, they were not successful in obtaining the desired properties of diamond films, since Raman spectra showed non-cubic diamond band presence.

Chemical composition of microwave plasma have influence diamond growth processes. In the case of heteroepitaxy, Si substrate is etched by a hydrogen-methane plasma creating species related to the ternary gas system C-H-Si. In the case of growth from C-H-N gas system the difference in growth defects were observed. [1].

In this report, we define lattice disorder as shifts of atoms from the positions in ideal lattice. Crystal growth starts at a nucleation stage during which formation of defects is inevitable. Diamond structure is the derivative of cubic face-centered lattice which coexists with hexagonal close packed lattice. The 111 twinning frequently appear during CVD growth and 111 stacking faults were observed with Transmission Electron Microscopy (TEM).

During development of microwave plasma CVD process the optimized process parameters enabled the growth of water-clear single crystals of cubic diamond. The growth under other regions of process parameter field yielded disordered tetrahedral structures. The discrete defects (stacking faults, twins, dislocations, foreign atoms, inclusions, interstitials, etc.) cause shifts of atoms in the lattice. In the case of diamond, the displacements in the interatomic distance are usually less than 2%. In this paper we show how X-ray diffraction revealed the disturbances of cubic diamond lattice symmetry.

The curved position sensitive detectors, introduced by Rigaku of Americas into X-ray diffraction practice in 2008, resulted in the increase in resolution, speed, and accuracy of intensity measurement of scattered X-rays comparing to photographic films. Imaging plate detector (IPD) has two-dimensional grid of pixels on the surface of a cylindrical screen to replace photographic film in the camera used for the rotation/oscillation crystal method [2]. To our knowledge, this study is the first report of diamond data using IPD detector. It is important to note that all CVD diamond crystals studied with IPD detector depart from cubic symmetry in contrast to the typical X-ray diffractometer data described in Kobashi book [3].

IPD measures intensity individually at each pixel, drastically improving the spatial resolution of the intensity function, because detector sensitivity is one X-ray photon per pixel. The intensity variation within Bragg reflections from a single crystal diamond is registered as a field image with changing grayness. Our reports are based on the analysis of such pixel images, i.e. reading pixel angular position and intensity. The scattering arising in the vicinity of reciprocal lattice points (rlps) as satellite spots is also registered in a manner described above.

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The ideal strictly periodic crystal lattice built of point-like atoms and described in the real space corresponds to the reciprocal lattice in a diffraction space. Such reciprocal lattice is used together with Ewald construction to explain x-ray diffraction experiments. The X-ray diffracted beams from crystal planes hkl have a form of peak intensity function at rlps. In other words, it looks like an array of Dirac delta functions. Such array represents Fourier transform of a periodic lattice [4]. We follow kinematical theory of X-ray diffraction in our study of diamond [5,6].

Scattering from a real crystal of silicon, considered in this study as X-ray diffraction standard, introduces some broadening of Bragg and stationary reflections due to Si crystal defects and instrumental broadening. The primary X-ray beam in our experiment is neither strictly monochromatic nor is ideally parallel. It means that our probe into the reciprocal space is not point-like; rather it has a finite volume, leading to the instrumental broadening. Despite of these facts, such probe is still satisfactory for study of CVD diamond crystals because they are inferior structurally compared to Si crystal. In other words, diamond Bragg reflections are more broaden than those of Si and have satellites, which do not appear for Si, which is considered as a nearly perfect crystal. The approach presented here describes the details of the function of scattering intensity registered in the vicinity of rlps, which are resolved due to the high resolution of IPD detector. We see the disturbance of the intensity function within and around Bragg reflections and the differences within the family of reflections corresponding to the equivalent hkl-indices; we call it the anisotropy of Bragg reflections.

The next step was focused on collecting of the diffraction data from relatively perfect natural diamond crystal, followed by the study of highly oriented diamond (HOD) film grown by CVD on (001) Si, and covered by thin film pattern of gold. This diamond film shows non-cubic 2.036 Å satellite to 111 cubic 2.056 Å diamond line.

Having diffraction patterns from Si, gold, natural diamond, CVD diamond film on Si we conducted a comparison to demonstrate considerable distortions of cubic lattice of CVD diamond crystals, and related it to Raman spectra. Thinking about practical application of CVD diamond single crystals we consider allowable departure from the strict lattice periodicity, keeping in mind Bloch theorem. Such properties, as electrical carrier transport, carriers' mobility, thermal conductivity, hardness, optical centers and many others, depend on the deviation from the strict periodicity of a diamond lattice. Displacement disorder of atoms is responsible for the status of thermal conductivity of diamond crystals, which varies in the wide range from low values for polycrystalline CVD films to extreme cases of isotopically pure single crystals. In diamond, heat flows through elastic waves, which propagation is attenuated when atomic displacements disturb periodic order. Understanding this atomic disorder could be an important help in progress of decreasing defects density.

In general diamond materials show lattice disturbances of many kinds. Polytypes, created during CVD process, are associated with hexagonal structure in combination with planar disorders. Polytypism appears in many phases like hexagonal diamond, ZnS, SiC, cobalt and others.

Using solely X-ray diffraction from disordered phases is not sufficient to conduct determination of atomic configurations of defects in these phases. Let's take an example of boron, which produces X-ray diffraction patterns that mimic single crystal while showing forbidden 5-fold symmetry in a particular crystallographic direction. We know that boron atoms are arranged in icosahedron sub-units, and we suspect that icosahedra can be arranged in quasi-crystal network or create nano-twinning, but today this problem is not solved, because we are lacking atomic resolution images from electron microscopy imaging techniques. The complicated X-ray patterns from β-rhombohedral boron still await for structure determination. Boron was considered as a candidate for electronic material, but it failed because of structural disorder.

The objective of this paper is to develop the X-ray diffraction method to detect lattice distortions of CVD diamond crystals. We have not pursued a goal to determine strict atomic configurations of growth defects models, which is a tremendous task by itself, because of the lack of atomic resolution in the case of diamond. Such determination requires a collaborative effort of many researchers to combine various characterization techniques. Currently, Scanning Tunneling Microscopy (STM) and High Resolution Transmission Electron Microscopy (HRTEM) do not provide sufficient resolution.

We suggest that the geometry of distribution of X-ray scattering intensity around rlps would serve as a practical gemological criterion for estimation of the quality and/or the indication of origin or method of growth of given diamond crystal.

2. Materials and methods

A natural diamond crystal (water-clear, originated from Siberia, kindly supplied by Dr. R. DeVries) used in this study had the shape of a regular octahedron and length of 1 mm along the edge. Its Raman spectrum resembled that of perfect diamond with sharp 1332 cm^{-1} peak (FWHM = 2.1 cm^{-1}) and the flat and low background with peak to background ratio of 1000.

Highly oriented diamond film on (001) Si, kindly supplied by Drs. Wolter and Kohn of Ulm University (Germany), was grown by microwave plasma CVD. The thickness of the film was 24 μm on a 0.4 mm substrate. Such thin film generates much weaker X-ray diffraction spots than natural diamond crystal. A pattern of thin film (0.5 μm) of gold was sputtered on the top surface. In present study the film was examined by optical and scanning electron microscopy (SEM).

The X-ray diffraction (XRD) experiments were conducted using RIGAKU D/MAX Rapid II x-ray diffractometer (Rigaku Americas Corporation, The Woodlands, TX). X-ray generator was run at 50 kV and 40 mA. Copper radiation was monochromatized using (002) reflection from flat graphite to Cu K α 1,2 lines, and passed through 0.1 or 0.3 mm circular beam collimators. The primary beam had a circular shape. The sample was mounted on a goniometer and oriented and centered using a CCD video camera. A cylindrical imaging plate area X-ray detector (IPD) had a radius of 127.4 mm. The measured 2θ range was from $-47°$ to $163°$ 2θ. The active image area was 470×256 mm. The pixel size was 100×100 μm and the sensitivity was 1 X-ray photon per pixel. The individual pixels measured incoming X-ray intensity independently. The distribution of X-ray scattered intensity was analyzed using Rigaku software.

In this study inspection of reciprocal space was conducted using two approaches: oscillation and stationary crystal methods. For the first method we browse a limited volume of reciprocal space. The primary X-ray beam lays in the equatorial plane and crossed the rotation axis. The ⟨110⟩ direction of Si and diamond crystals were parallel to the rotation axis, and the ω angles were in equatorial plane. The schematic for the oscillation pattern is shown in page 85 of reference [2]. The oscillation patterns have been recorded for variety of ω angle ranges.

The stationary crystal patterns were taken at fixed ω positions for rlp relatively close to Ewald sphere. If a reflection falls outside Bragg reflection, we call it “satellite reflection”. The stationary images have been registered at ω angles corresponding to Bragg position and at several shifts from the Bragg position. The set of stationary images allows construction of pseudo “rocking curve”. Note that “rocking curve” term is normally used for double crystal diffractometer.

3. Experimental results anddiscussions

3.1. Comparison of X-ray diffraction spots from silicon and natural diamond single crystals

The enlargements of Bragg reflections from oscillation patterns and diffraction spots from stationary images are shown below to visualize the grid of pixels pattern. The intensity of the spots is shown in grey