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Hydrogen analysis of BCN films with resonant nuclear reactions

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Abstract

Hydrogen is one of typical contaminants in carbon-based films. It can strongly influence the mechanical, physical and chemical properties of the films. The analysis of hydrogen is therefore a crucial problem in the course of preparing the films with the required properties. Ion beam techniques using nuclear reactions are effective for the quantitative determination of hydrogen concentration. A specially designed spectrometer is employed for the detailed determination of hydrogen concentrations by detecting 4.43 MeV γ-rays from the resonant nuclear reactions $^{1}H(^{15}N,\alpha\gamma)^{12}C$ at 6.385 MeV. In this study, the BCN films were formed on silicon substrate with ion-beam-assisted deposition (IBAD), in which boron and carbon were deposited by electron beam heating of B_4C solid and nitrogen was supplied by ion implantation simultaneously. The hydrogen depth profiling in the near surface region of BCN films were performed by employing RNRA. The mechanical properties of BCN films were evaluated using an ultra-micro-hardness tester. It has been confirmed that the hardness of BCN films becomes larger with the increase of the hydrogen concentration.

Keywords: BCN film; IBAD; Hardness; RNRA; Hydrogen; TRIM

1. Introduction

The mechanical features of materials coated with diamond-like carbon (DLC) thin films are strongly influenced by the chemical bonding state at the interface between DLC films and the substrate. The DLC films on nonferrous materials such as aluminum alloys can improve their mechanical properties greatly but the adhesion to the substrates is not good enough so as to be used as cutting tools. The ion beam mixing techniques have been examined to improve the adhesion of DLC films in this nonferrous system [1,2].

On the other hand, the adhesion of DLC films is excellent to ferrous materials, which has been utilized mainly in the industrial applications. It has been recognized that if DLC films are used for the frictional components, the life of DLC films can be shortened because of the high diffusion rate of carbon at high temperature during the operation conditions. On the contrary, the impurity doping with B and N can be reasonably expected to realize the excellent slide characteristics, and BCN films have been synthesized on silicon wafer substrates by ion-beam-assisted deposition technique (IBAD). It has been observed that the BCN films were tougher than DLC films in the adhesion test even if the friction coefficient is low [3].

For further extended applications in the industries, the BCN films should have superior characteristics in the mechanical properties such as hardness, friction and adhesion to substrate.

The influences of hydrogen impurities on the mechanical properties such as hardness of DLC and BCN films are also supposed to be so significant due to the breaking down of sp^3 bonding network by the hydrogen introduction. The hydrogen doping into carbon-related films is not necessarily uniform along the depth, and it has become important to evaluate the depth profile of hydrogen atoms especially in the mechanical components by employing a nondestructive technique. Until now, we have carried out the hydrogen analysis by employing the elastic recoil detection analysis

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(ERDA) method, in which the energies of hydrogen atoms recoiled by incident high-energy heavy ions are analyzed in order to quantitatively evaluate the hydrogen distribution in DLC films [4]. However, in this technique, the sample should have large uniform area because the incident angle and also the detection angles are very low as around 15°.

In the present paper, the results of hydrogen profiling in BCN based on the resonant nuclear reaction analysis (RNRA) method are described [5]. Moreover, the relation between hydrogen concentration and hardness in BCN films is also shown.

2. Experimental

2.1. Deposition machine

Fig. 1 shows a schematic diagram of the main components of the IBAD system, which consists of the electron beam evaporator and the ion implanter with a microwave discharge ion source. Both the evaporator and the target are water-cooled. The electron beam evaporated deposition (EBED) and the implantation conditions are listed in Table 1. The target materials used are boron carbide (B_4C) blocks.

2.2. Formation of BCN films

When the electron beam strikes B_4C blocks, B and C elements are evaporated and deposited on a substrate, and concurrently N ions are implanted in the substrate. The films and their formation conditions are listed in Table 2. The thickness of BCN films measured by scanning laser microscope is 0.3–0.4 μm.

2.3. Hydrogen implantation into BCN films

The 20-keV hydrogen ions were implanted into the BCN film perpendicularly. The detailed conditions of hydrogen ion implantation are shown in the Table 2. The doses of hydrogen ions were 8×10^{16}, 2×10^{17}, and 5×10^{17} ions/cm^2. Though the fraction of ionized hydrogen in a microwave ion source can be changed depending on the incident electric power, it is supposedly reasonable that the concentrations of H^+ and H_2^+ ions are almost the same at 500 W judging from our many kinds of experiences [6].

2.4. Hydrogen profiling by RNRA

The resonant nuclear reactions with the sharp energy width can be used to obtain the detailed profiles of hydrogen atoms by detecting γ-rays as a function of incident energies of ^{15}N for example. The ^{1}H(^{15}N,αγ)^{12}C nuclear reactions at the incident energy of 6.385 MeV ^{15}N yield 4.43 MeV γ-rays [7]. In our study, RNRA was performed using a 3-MV tandem accelerator in TIARA/JAERI-Takasaki. The induced γ-rays were detected with a NaI detector, positioned as close as possible to a vacuum chamber, about 0.02 m in this. The resonance energy of ^{15}N at the surface was determined using the hydrogen-terminated Si target at first, and at the latter stage the energy calibration was carried out on samples with naturally adsorbed H_2O molecules. To probe hydrogen atoms inside the target, the ^{15}N energy is increased from the resonant energy step by step. The gamma ray yields were recorded at the step of 10 keV from 6.4 to 6.8 MeV. The typical dose required for the reasonable statistics of gamma-ray yields was about 2 μC per data point, but it was adjusted depending on the hydrogen content in a sample.

2.5. Measurement of hardness

The hardness of BCN films was measured using the Dynamic ultra-micro-hardness tester (Shimadzu) at a load of 9.8 mN with a Vickers' indenter and at a loading speed of 4.8×10^{-2} mN/s. The thickness of deposited layers are thin

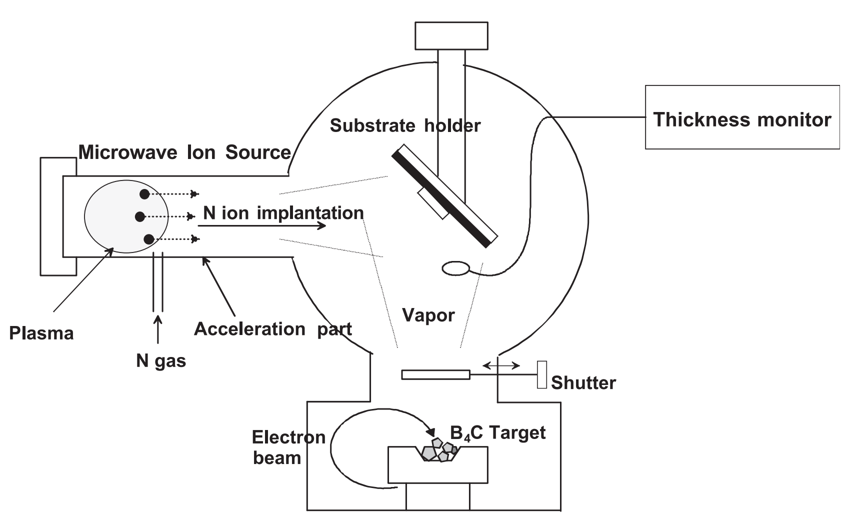

Fig. 1. Schematic illustration of the IBAD system composing of the ion-beam implanter and the electron beam evaporator.