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Study of diamond films synthesized on Si substrates by monoenergetic positron beams

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Monoenergetic positrons were used as a nondestructive probe for diamond films synthesized on Si substrates from a gas phase of a CH_4/H_2 mixture by microwave plasma chemical vapor deposition. Doppler broadening profiles of the annihilation photons and lifetime spectra of positrons were found to be sensitive for vacancy-type defects in the diamond films. From the measurements, the annihilation of positronium atoms (Ps) trapped by vacancy-type defects was observed. The formation probability of Ps and its lifetime were found to increase with increasing the concentration of CH_4. This suggests that the concentration of voids and its volume increase with increasing the concentration of CH_4.

1. INTRODUCTION

The nature of diamond and diamond-like carbon films deposited on diamond or other substrates has been extensively studied for their unique properties, e.g., extreme hardness, chemical resistance, high dielectric strength, optical transparency, large band gap, high electrical resistivity and high thermal conductivity [1-7]. The characterization of the synthesized diamond has been based on measurements of optical and electrical properties, and x-ray and electron beam analysis. The positron annihilation technique is now a powerful method for the study of defects in metals and semiconductors [8]. A positron implanted into the specimen eventually annihilates with an electron producing two annihilation γ rays. The Doppler broadening spectrum of such annihilation γ rays provides the momentum distribution of the annihilating electrons. Since a positron is positively charged, it is repelled from ion cores by a Coulomb interaction. Thus, if a specimen contains vacancy-type defects, there is a finite probability of positrons being trapped in these regions. Due to a reduced overlap of positrons with core electrons in vacancy-type defects and a reduced electron density in such defects, the electron-positron momentum distribution narrows and the lifetime of trapped positrons increases. Thus, from measurements of Doppler broadening profiles or those of lifetime spectra, one can detect vacancy-type defects.

The development of variable-energy positron beams has demonstrated that monoenergetic positrons can be successfully utilized as a nondestructive surface and subsurface probe [9]. The acceleration of such slow positrons makes it possible to adjust the implantation profile of positrons to restricted regions of interest in the specimen. Therefore, by measuring the Doppler broadening profiles or lifetime spectra as a function of the incident positron energy, one can detect defects under the subsurface region. In the present paper, we report the application of the monoenergetic positron beams to the study of defects in diamond films synthesized on Si substrates by microwave plasma chemical vapor deposition (CVD).

2. EXPERIMENTAL

The specimens used in the present experiment were polycrystalline diamond films synthesized on Si(111) substrates (0.01 Ωcm n-type) by microwave plasma CVD. The microwave power was 500 W. The pressure of the CH_4/H_2 mixture was 4 kPa. The concentration of CH_4 was varied from 0.1 to 3.0 volume%. The period of the growth was 48 to 100 hours. The thickness of the diamond films, d, was measured by scanning electron microscope (SEM) for the specimen with the CH_4 concentration of 0.1 volume% as d=0.8±0.1 μm, for 1.0 volume% as d=1.4±0.1 μm, for 3.0 volume% as d=0.7±0.1 μm, respectively. The densities of the diamond films were 3.5 g/cm^3 for the specimens with 0.1 and 1.0 volume%, and 3.2 g/cm^3 for the specimen with 3.0 volume%.

The monoenergetic positron beam line installed at the University of Tsukuba was used for the present experiment [10]. Doppler broadening profiles of the annihilation radiation were measured by a Ge detector as a function of incident positron energy. The observed annihilation spectrum was characterized by the S parameter [8]. The pulsed monoenergetic positron beam line constructed at the Electrotechnical Laboratory was used in order to measure lifetime spectra for the diamond films. The detail of the system was described elsewhere [11].

The lifetime spectrum for a single-crystal diamond synthesized at high pressure was also measured by a fast-fast system using a ^{22}NaCl positron source with a strength of 8x10^5 Bq deposited on kapton foils. This measurement was performed with BaF_2 scintillators attached to XP2020Q (Philips) photomultiplier tubes. All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the S parameter as a function of the incident positron energy, E, for the diamond films synthesized on the Si substrates by microwave plasma CVD under different CH_4 concentrations. For the specimen grown with the CH_4 concentration of 0.1 volume%, the value of S was found to be nearly constant at high incident positron energy (E≅30 keV). This means that almost all positrons implanted with this energy range annihilate in the Si substrate. In the region of E between 6 keV and 9 keV, the S-E plots were found to be nearly flat for all specimens. This means that these values of S correspond to the annihilation of positrons in the diamond films. It was also found that these characteristic values of S for the diamond films drastically increased with increasing the concentration of CH_4. The change in the value of S was about 30 % with increasing CH_4 concentration from 0.1 volume% to 3.0 volume%. For Si specimens, the change in the value of S due to the trapping of positrons by vacancy clusters is about 5% [12]. Therefore, the observed drastic increase in the value of S can not be attributed to the annihilation of positrons trapped by vacancy-type defects in the diamond films.

In order to know the annihilation characteristics of positrons in the diamond films, lifetime spectra of positrons were measured at E=6 keV by using the pulsed monoenergetic positron beam. From the results shown in Fig. 1, almost all positrons are considered to annihilate in the diamond film

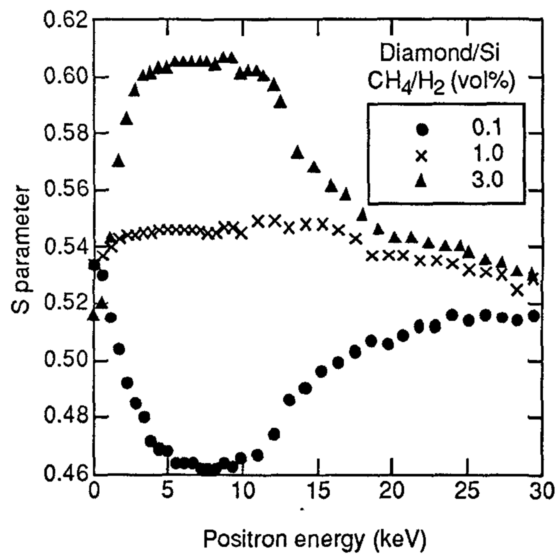

Figure 1. The line shape parameter S as a function of the incident positron energy for the diamond films synthesized on the Si substrates by microwave plasma CVD under different CH_4 concentrations.

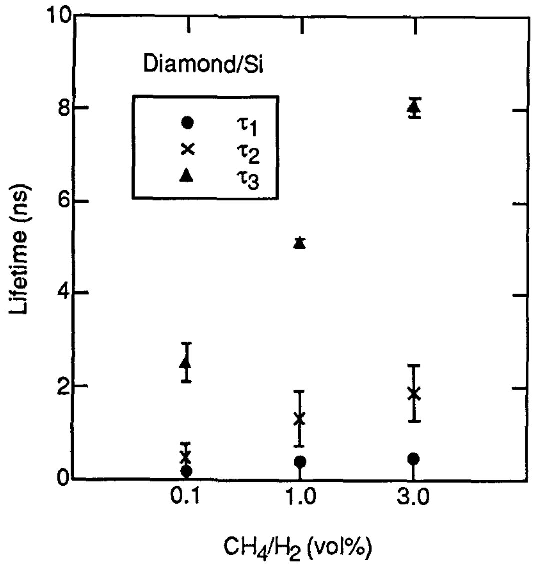

Figure 2. The lifetime for the diamond films synthesized on the Si substrates by microwave plasma CVD under different CH_4 concentrations.

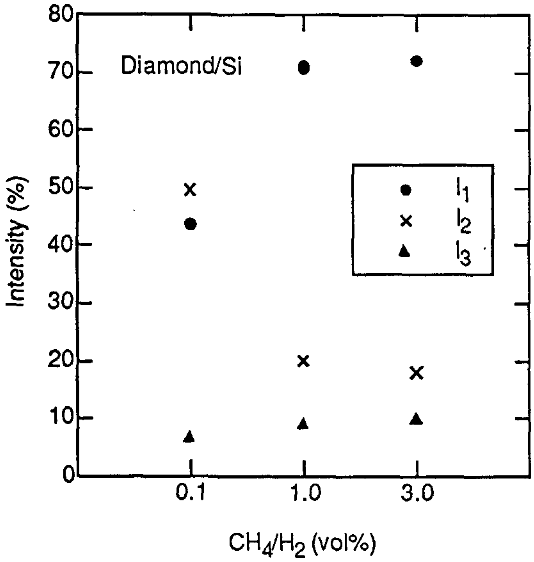

Figure 3. The intensity for the diamond films synthesized on the Si substrates by microwave plasma CVD under different CH_4 concentrations.

at this energy. Figures 2 and 3 show the lifetimes and their intensities for each specimen. For the diamond films grown with the CH_4 concentration of 1.0 and 3.0 volume%, the second and the third lifetime were found to range between 1 ns and 8 ns (Fig. 2). These values are longer than the typical lifetime of positrons in crystalline solids; for example, the lifetime of positrons in a bulk Si is 220 ps and that in vacancy-type defects in Si ranges between 270 ps and ~500 ps (ref. 13). Therefore, the observed second and the third components can not be associated with the annihilation of positrons trapped by vacancy-type defects.

A positronium (Ps) atom, a hydrogen-like bound state between a positron and an electron, may form in void or pores [14]. Ps exhibits two spin states which are called "para-Ps" and "ortho-Ps" for the singlet state and the triplet state, respectively. The intrinsic lifetime of para-Ps is ~125 ps and that of ortho-Ps is ~140 ns. In condensed materials, however, the lifetime of ortho-Ps is only 1~5 ns because the positron can annihilate with one of the surrounding electrons rather than its own partner. This process is called "pick-off" annihilation of ortho-Ps [14]. Thus, the observed second and the third components in the diamond films can be associated with the pick-off annihilation of ortho-Ps. The lifetime of positrons for the single-crystal diamond synthesized at high pressures was 115.2±0.4 ps, and no component associated with the annihilation of Ps was observed. This result suggests that positrons in the bulk diamond annihilate only from the free state. Thus, the second and the third components for the diamond films grown with the CH_4 concentration of 1.0 and 3.0 volume% can be attributed to the pick-off annihilation of ortho-Ps trapped by voids. The values of τ_3 and I_3 were found to increase with increasing the concentration of CH_4 (Figs. 2 and 3). This suggests that the size and the concentration of such voids increase with increasing the concentration of CH_4.

Since the annihilation from the para-Ps state produces two γ-rays with very narrow energy width, the formation of para-Ps increases the value of the S parameter. Thus, the drastic increase in the value of S for the diamond films with high

CH_4 concentration can be attributed to the increased formation probability of Ps.

From the observed lifetime of ortho-Ps, one can estimate the size of voids [15]. By using the value of τ_3, the diameters of voids were calculated as 0.7, 1.0 and 1.2 nm for the diamond films grown with the CH_4 concentration of 0.1, 1.0 and 3.0 volume%, respectively. By using the value of τ_2, they were calculated as 0.4 and 0.6 nm for the diamond films at 1.0 and 3.0 volume%, respectively. For the diamond film grown with the CH_4 concentration of 0.1 volume%, because of the value of τ_2 (470 ps), the second component may be associated with the annihilation of positrons trapped by vacancy-clusters.

4. CONCLUSIONS

We have used monoenergetic positrons to characterize the diamond films on the Si substrates synthesized from the gas phase of the CH_4/H_2 mixture by microwave plasma CVD. The high formation probability of Ps was found from the measurements of the Doppler broadening profiles and those of the lifetime spectra of positrons for the specimen grown with the CH_4 concentration of 3.0 volume%. The vacancy-type defects with high concentration still exist in the film deposited at the CH_4 concentration of 0.1 volume%. The sizes of voids in the diamond films were estimated from the observed lifetimes of ortho-Ps trapped by such defects. The present investigation shows that positrons provide a sensitive and nondestructive probe for the characterization of diamond films grown on Si substrates.

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