I-1. PROJECT RESEARCHES

Project 3

PR3 Enhancement of research methods for material irradiation and defect analysis

A. Kinomura

Institute for Integrated Radiation and Nuclear Science, Kyoto University

OBJECTIVES: Irradiation facilities of high-energy particles for neutrons (Material Controlled irradiation Facility), ions (e.g., Heavy ion irradiation facility) and electrons (Temperature-controlled irradiation facilities of KUR-LINAC) have been extensively developed at the Institute for Integrated Radiation and Nuclear Science. The developed facilities have been in operation and opened for joint research projects. One of the objectives of this project is to further improve or optimize irradiation facilityies for advanced irradiation experiments.

As characterization techniques for irradiated materials, a slow positron-beam system and a focused ion beam system have been developed and introduced, respectively, in addition to previous characterization facilities such as an electron microscope, an electron-spin-resonance spectrometer, a bulk positron annihilation spectrometer and a thermal desorption spectrometer. Another objective is to introduce new experimental methods or reconsider analytical methods of previously used characterization techniques.

Based on these two objectives, we expect the enhancement of previous studies and the attraction of new users for the joint research program.

The allotted research subjects (ARS) and co-researchers are listed below. The titles of research subjects are taken from the individual reports.

ARS-1:
Study to improve transport and measurement performance of a slow positron beamline (A. Kinomura et al.)
ARS-2:
Doping effect of Cr, Mo, Ta, and Re on defect formation after electron irradiation (T. Toyama et al.)
ARS-3:
Hydrogen Thermal Desorption Analysis in Electron-irradiated F82H (K. Sato et al.)
ARS-4:
Gamma-ray induced photo emission from ZnO single crystal wafer: Comparison with GaN (T. Nakamura et al.)
ARS-5:
Irradiation technique for study on corrosion resistance of fusion divertor materials to liquid metal during irradiation (M. Akiyoshi et al.)
ARS-6:
Investigation of free volume in diamond like carbon films deposited by various methods (K. Kanda et al.)
ARS-7
Positron annihilation spectroscopy on diamond-like carbon films (S. Nakao et al.)

RESULTS:

In ARS-1, a brightness enhancement system have been developed for the KUR slow positron beamline as well as measurement systems for positron annihilation lifetime spectroscopy. In this year, positron annihilation lifetime measurements were successfully demonstrated with a brightness enhanced beam in the KUR slow positron beam system. A spot size evaluated by a knife edge method using sample edges was 2.3 mm (FWHM).

In ARS-2, electron irradiation to pure W, W-5%Re (in weight %), W-0.3%Cr, W-1.5%Mo, and W-5%Ta was performed at LINAC at KUR at 8 MeV. After electron irradiation, the average lifetime increased, showing positron trapping to vacancy type defects. Average lifetimes for W-0.3%Cr and W-5%Re remained relatively short compared with the W-1.5%Mo and W-5%Ta alloys, suggesting that the formation of irradiation induced defects was suppressed.

In ARS-3, the TDA of electron-irradiated F82H was conducted after electrolysis hydrogen charging. The hydrogen atom trapping sites in materials were investigated using simulation program for TDA. The TDA curve of electron-irradiated F82H showed a main peak around 320 K and a shoulder peak from 370 K to 420 K. The simulation curve corresponds well to the experimental one except for the shoulder around 420 K.

In ARS-4, although ZnO and GaN have the wurtzite structure and direct bandgap with almost the same bandgap values, peak intensities of the gamma-ray induced photo emission were different. It is considered to be due to the difference in the light emitting mechanism between YL of GaN and GL of ZnO.

In ARS-5, the planned experiments were not performed this year for the influence of infectious disease countermeasures.

In ARS-6, S parameters showed good correlation with film density and hardness. As the density and hardness decrease, the S parameter increases, since the increase in S parameter is considered to mean the increase in free volume. Positron lifetimes increased with decreasing of the density and hardness as well. On the other hand, it was found that the S parameter and positron lifetime have no direct correlation to the hydrogen content estimated from ERDA or NEXAFS measurements.

In ARS-7, Si-DLC and Si-PLC films were deposited on Si substrates by a bipolar-type plasma-based ion implantation and deposition (PBII) system, followed by annealing at 400 ^{o}C and 800 ^{o}C in vacuum to investigate the thermal stability of the films. The results of positron annihilation spectroscopy suggested that Si incorporation may promote to increase porosity in the films and prevent structural changes due to H release by ion bombardment or thermal annealing at high temperature.

SUMMARY: Several new irradiation (electron-beam and gamma-rays) and analytical (slow-beam and conventional positron measurements) techniques for various materials have been developed and improved for the objectives of this project. Such studies may enhance developments of new techniques and materials research on irradiation effects.

PR3-1 Study to improve transport and measurement performance of a slow positron beamline

A. Kinomura, N. Oshima[1], A. Uedono[2] and A. Yabuuchi

Institute for Integrated Radiation and Nuclear Science, Kyoto University
[1]National Institute of Advanced Industrial Science and Technology (AIST)
[2]University of Tsukuba

INTRODUCTION: Positron annihilation spectroscopy is an important analytical method to detect vacancy-type defects and vacant spaces of materials. Energy-variable mono-energetic positron beams (slow positron beams) are essential to perform depth-dependent positron annihilation spectroscopy of surface layers such as ion-implanted layers or thin films formed on substrates. Intense positron sources are necessary to obtain slow positron beams for practical use. In general, positron sources based on pair creation can provide higher intensity than radioisotope-based positron sources. A positron source using pair-creation by gamma-rays from a nuclear reactor have been developed by using Kyoto University research Reactor (KUR) to obtain a slow positron beam for materials analysis. In the KUR slow positron beamline, the source size (converter and moderator assembly) is approximately 30 mm in diameter. For typical sample sizes of materials analysis ($\leq$10 mm), it is necessary to reduce beam sizes efficiently while keeping beam intensity as high as possible. For this purpose, a brightness enhancement system have been developed for the KUR slow positron beamline [1]. In addition, measurement systems for positron annihilation lifetime spectroscopy have been optimized in this study.

EXPERIMENTS: In previous studies, the brightness enhancement system of the KUR slow positron beam line has been evaluated using beam-spot images on phosphor screens attached to microchannel plates. In addition, a knife-edge method using a brightness enhanced beam was examined over samples edges with Doppler broadening measurements. During the brightness enhancement operation, a positron pulsing system and a sample holder need to be biased with an extraction voltage (typically 5 keV). As pulsing signals are required for the lifetime measurement circuit located at the ground state (0 V), pulsing signals were transported through an isolation transformer from the high voltage state to the ground state.

RESULTS: After the positron pulsing system with a normal setup [2] was optimized for a Kapton sheet at 2 keV, the brightness enhancement system was then operated. The Ni re-moderator was inserted in the beam trajectory and additional optics with a magnetic lens and solenoid coils were excited. An extraction voltage of the beam from the Ni re-moderator was 5 keV. As a result, the high voltage of the sample was adjusted to 7 keV to obtain an acceleration voltage of 2 keV.

Fig. 1 shows the positron annihilation lifetime spectra of the Kapton sheet measured with and without the brightness enhancement (B.E.) system. A satellite peak around 8 ns in Fig. 1(a) is one of the background peaks corresponding to the bunching period of the pulsing system. On the other hand, no satellite peak was observed around 8 ns in fig. 2(b). This difference is attributed to the narrower energy spread of the brightness enhanced beam.

Fig. 2 shows the result of position-dependent intensities of the Kapton lifetime component. The positron beam was moved across the edges of a YSZ sample placed on the Kapton sheet. The positron lifetime spectra were collected at each position. The intensities of the lifetime component of the Kapton was plotted. This procedure can be used as a knife-edge method. The fitting of a Gauss function gave a spot size of 2.3 mm (Full width half maximum: FWHM).

In summary, positron annihilation lifetime measurements were successfully demonstrated with a brightness enhanced beam in the KUR slow positron beam system. A spot size evaluated by a knife-edge method using sample edges was 2.3 mm (FWHM).

REFERENCES:

[1] Y. Kuzuya *et al.* J. Phys. Conf. Series 791 (2017) 012012.
[2] M. Nakajima *et al.* Rev. Sci. Instrum. 91 (2020) 125109.

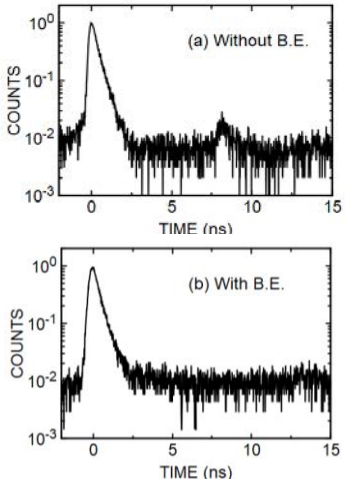


Fig. 1 Positron annihilation lifetime spectrum of a Kapton sheet measured without (a) and with (b) the brightness enhancement system.

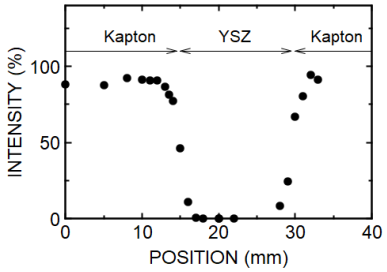


Fig. 2 Position depnedence of intensities of the Kapton lifetime component across sample edges.

PR3-2 Doping effect of Cr, Mo, Ta, and Re on defect formation after electron-irradiation

T. Toyama[1], Y. Hatano[2], T. Suzudo[1], A. Yabuuchi[3], A. Kinomura[3], K. Inoue[1], Y. Nagai[1]

[1]*Institute for Materials Research, Tohoku University*
[2]*Organization for Promotion of Research, University of Toyama*
[3]*Institute for Integrated Radiation and Nuclear Science, Kyoto University*

INTRODUCTION: Tungsten (W) is a first-candidate material as plasma-facing materials for fusion reactors thank to its high melting point, high sputtering resistance to energetic particles, and the very low solubility of hydrogen isotopes which is a notable advantage in reducing tritium (T) retention. However, recent studies have reported that neutron-irradiation and ion-irradiation cause significant enhancement of hydrogen isotope retention in W, due to hydrogen trapping at irradiation-induced defects such as vacancies, vacancy clusters, and dislocation loops. Recently it was found that the addition of rhenium (Re) to W drastically reduces the hydrogen isotope accumulation [1]. As a mechanism for this, quantum chemical calculation has been performed [2]; it is suggested that Re is strongly bound to interstitial atoms, so that recombination of interstitial atoms and vacancies is promoted, and the formation of vacancy-type defects that become hydrogen capture sites is suppressed. However, no experimental studies on this have been obtained. In this study, we performed electron-irradiation to introduce only a simple Frenkel pair to W or W-Re alloy. The effect of Re addition on the defect formation is investigated by the positron annihilation method. In addition, the effect of Cr, Mo, and Ta is investigated as well.

EXPERIMENTS: Electron-irradiation to pure W, W-5%Re (in weight %), W-0.3%Cr, W-1.5%Mo, and W-5%Ta was performed at LINAC at KUR at 8 MeV, at temperature of < 100 ℃ to the fluence of ~4E+23 e^-/m^2. Positron annihilation measurements (lifetime measurement and coincidence Doppler broadening measurement) were performed.

RESULTS: Figure 1 shows results of average positron lifetime before and after electron-irradiation for the samples. In pure W, the average lifetime was about 120 ps before electron-irradiation, which is close to the value in W bulk. After electron-irradiation, the average lifetime increased, showing positron trapping to vacancy-type defects induced by electron-irradiation. In W-1.5%Mo and W-5%Ta alloys, the trends were almost similar to that for pure W, indicating that the effect of these elements on the formation of irradiation-induced defects are not significant. In contrast, the average lifetime for W-0.3%Cr and W-5%Re remained relatively short compared with the other alloys, suggesting that the formation of irradiation-induced defects was suppressed. The possible candidate for positron trapping site for W-0.3%Cr and W-5%Re after irradiation could be dislocations in which positron life-time value may be shorter than mono-vacancy. Figure 2 shows the deuterium (D) retention in W and W alloys before/after 6.4 MeV Fe ion irradiation at DuET at Kyoto University. For pure W, W-2.5Mo, and W-5Ta, significant increases in D retention were observed, which is attributed to the irradiation-induced defects after ion irradiation. On the other hand, the increase in D retention after irradiation was not significant for W-0.3%Cr and W-5%Re. This is due to the suppression of defect formation after irradiation, which is well-confirmed by the present positron lifetime measurements shown in Fig. 1.

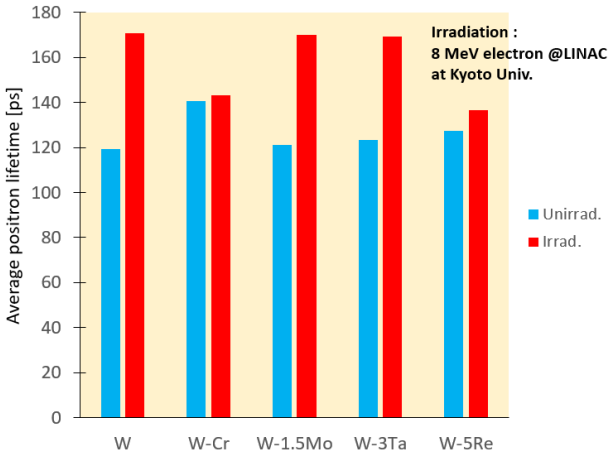


Fig. 1 : Average positron lifetime in W alloys before/after electron irradiation at LINAC.

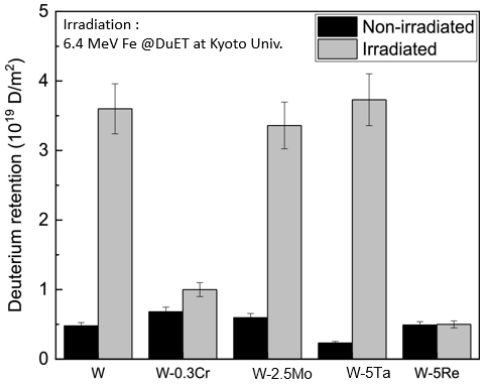


Fig. 2 : Deuterium retention in W alloys before/after 6.4 MeV Fe ion irradiation (Reproduced from J. Wang et al., J. Nucl. Mater. **545** (2021) 15274) .

REFERENCES:

[1] Y. Hatano *et al.*, Nucl. Mater. Energy **9** (2016) 93.
[2] T. Suzudo, A. Hasegawa, Sci. Rep. **6** (2016) 36738.
[3] J. Wang *et al.*, J. Nucl. Mater. **545** (2021) 152749.

PR3-3 Hydrogen Thermal Desorption Analysis in Electron-irradiated F82H

K. Sato, T. Kamimura, S. Komazaki, Q. Xu[1], A. Yabuuchi[1], A. Kinomura[1]

Graduate School of Science and Engineering, Kagoshima University
[1]Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: Thermal desorption analysis (TDA) is widely used to identify the gas atom trapping sites in the field of spallation neutron source materials [1], fusion reactor materials [2] and hydrogen embrittlement [3] and so on. To know the interaction between gas atoms and defects, which has an influence on microstructural evolution, is very important to develop the performance of their materials. TDA curves change if defects grow in the material (size or density change). Therefore, using the TDA, Komazaki et al. detected the formation and growth processes of defects during creep test of high Cr ferritic steels, and estimated the remaining life of the structural materials [4, 5].
In TDA, to obtain the binding energy of gas atoms to defects, three experiments under different rate of temperature increase should be performed [6]. However, it is often difficult to prepare multiple samples irradiated in spallation neutron sources or fusion reactors under same irradiation condition. Therefore, the simulations were also carried out to identify the gas atom trapping sites [2, 7]. In this study, the TDA of electron-irradiated F82H was conducted after electrolysis hydrogen charging. The hydrogen atom trapping sites in materials were investigated using simulation program for TDA.

EXPERIMENTS AND SIMULATIONS: IEA heat F82H [8] was used in this study. Disk samples with a dimeter of 5 mm and thickness of 0.5 mm were fabricated using a wire electric discharge machine. Defects were introduced by irradiation with electrons at 8 MeV using the electron linear accelerator of Institute for Integrated Radiation and Nuclear Science, Kyoto University. The irradiation temperature was 333 ± 10 K, and irradiation dose was 1.4×10^{-4} dpa. Hydrogen was charged to the samples using a cathodic electrolysis charging method; also, 0.1 mol/L NaOH with 0.5 mass% NH_4SCN was used. The current density and the charging temperature were 50 A/m^2 and 303 K, respectively. The charging time was for 4 h. The hydrogen molecules were counted at intervals of 5 min using a gas chromatograph, and the system was calibrated with a standard mixture of hydrogen and argon gas with a heating rate of 100 K/h. Simulation program for TDA developed by Kamimura et al. [9] was used in this study.

RESULTS: In unirradiated F82H, when we used the values obtained in the previous study (hydrogen migration energy of 0.145 eV, the defect density of 1.6×10^{23} /m^3 (1.9×10^{-6}), and binding energy of 0.580 eV) [10] (case 1), the density was too low and the binding energy was too high to fit the simulation curve to the experimental one. When we used the hydrogen migration energy of 0.145 eV, the trapping site density of 4.65×10^{24} /m^3 (5.52×10^{-5}), and binding energy of 0.373 eV (case 2), the curve fitted to the experimental one was obtained. It is expected that trapping sites are interface of precipitates, dislocations, and block/packet/lath boundaries. Jia et al. observed dislocations of approximately 10^{14} /m^2 (density of atoms which compose dislocation core: 8.2×10^{-6}) by transmission electron microscopy in F82H [11]. Therefore, the defect density of 1.6×10^{23} /m^3 (1.9×10^{-6}) in the previous work [10] is too low. The hydrogen migration energy in α-Fe of 0.058 eV [12] is lower than that in F82H. As F82H includes many kinds of solute atoms, they capture hydrogen atoms, and slow the diffusion of hydrogen in F82H [13].
In the experimental TDA curve of electron-irradiated F82H, we can see a main peak around 320 K and a shoulder peak from 370 K to 420 K. The hydrogen migration energy, density, and binding energy of pre-existing defects were the same as case 2. The irradiation-induced defect is identified by positron annihilation lifetime measurements, di-vacancies were formed, and their density was 3.03×10^{-5}. The binding energy of hydrogen to vacancy clusters changes with the occupancy of hydrogen [14] and this changed according to the equation: $E_b = -0.631\theta^2 + 0.110\theta + 0.628$ (eV) (θ: occupancy of hydrogen to vacancy clusters). When the defect density is assumed as constant during the temperature increase, the curve does not fit to the experimental one. Therefore, it is assumed that the density of vacancy clusters monotonically decreases with increasing the annealing temperature. The simulation curve corresponds well to the experimental one except for the shoulder around 420 K. If the growth of the vacancy clusters is considered, better fitting curves will be obtained.

REFERENCES:
[1] B.M. Oliver *et al.*, J. Nucl. Mater. 356 (2006) 148.
[2] M. Poon *et al.*, J. Nucl. Mater. 374 (2008) 390.
[3] T. Nagase *et al.*, ISIJ Int. 58 (2018) 349.
[4] S. Komazaki *et al.*, Tetsu-To-Hagane, 96 (2010) 614.
[5] H. Yamashita *et al.*, Tetsu-To-Hagane, 102 (2016) 630.
[6] C.D. Doyle *et al.*, J. Appl. Poly. Sci. 5 (1961) 285.
[7] Y. Oya *et al.*, J. Nucl. Mater. 461 (2015) 336.
[8] A. Hishinuma *et al.*, J. Nucl. Mater. 258-263 (1998) 193.
[9] T. Kamimura *et al.*, Mater. Sci. Forum, 1024 (2021) 135.
[10] E. Serra *et al.*, J. Sci. Commun. 163 (2000) 51.
[11] X. Jia and Y. Dai, J. Nucl. Mater. 318 (2003) 207.
[12] W. Beck *et al.*, Proc. Royal Soc. A 290 (1966) 220.
[13] H.S. Zhou *et al.*, J. Nucl. Mater. 455 (2014) 470.
[14] J. Maisonneuve *et al.*, Fusion Sci. Tech. 60 (2011) 1507.

PR3-4 Gamma-ray induced photo emission from ZnO single crystal wafer: Comparison with GaN

T. Nakamura[1], T. Nishimura[1], K. Kuriyama[1], Atsushi Kinomura[2]
[1]*Research Center of Ion Beam Technology, Hosei University, Koganei, Tokyo 184-8584, Japan*
[2]*Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori, Osaka 590-0494, Japan*

INTRODUCTION: Emission characteristics for native and radiation induced defects of wide-gap semiconductors such as ZnO and GaN have been studied by cathode-luminescence using an electron beam and photoluminescence using a He–Cd laser. We recently observed gamma-ray induced photo emission from GaN single crystal wafers [1]. This observed emission corresponds to yellow luminescence (YL). We have also reported that the high resistive ZnO bulk single crystals became low resistive due to the Zn interstitials induced by gamma-ray irradiation of 170 kGy [2]. Whether the luminescence by the excitation of gamma rays is observed in ZnO is important as it may be used as an application as a gamma ray detector. The gamma-ray generates a Compton electron, causing the material to undergo internal bombardment by MeV electrons [3].

EXPERIMENTS: Undoped ZnO single crystal wafers with a size of 1 cm square and a thickness of several 100 μm meters were used for the present study. The resistivity measured by van der Pauw method was 104 Ω cm for an un- irradiated ZnO and varied to 30 Ω cm for ZnO irradiated with the total gamma-ray dose of 170 kGy [2]. Therefore, the resistance change of the ZnO crystal does not occur in the short-time during gamma-ray irradiation emission measurement of about 20 min, corresponding to the gamma-ray dose of ~0.59 kGy. That is, short-time irradiation will not produce detectable lattice defects. The crystals were irradiated at room temperature with gamma-rays of 1.17 and 1.33 MeV from a cobalt-60 source of Institute for Integrated Radiation and Nuclear Science, Kyoto University. The gamma-ray irradiation induced photo emission measurements were performed by using a charge coupled device (CCD) equipped spectrometer (QE Pro, Ocean Insight Co. Ltd.). Each measurement was performed under 20 min, gamma-ray irradiation and each spectrum was acquired for 2 min, CCD exposure time.

RESULTS: Fig. 1 shows the gamma-ray induced photo emission spectra of ZnO and GaN single crystal wafers. These spectra were measured at room temperature by the absorption dose rate of about 1.4 kGy/h using wafer thickness of 0.5 mm for ZnO and 0.25 mm for GaN. The GL peak in- tensity of ZnO is about 1/60 of gamma-ray induced YL observed in GaN single crystal wafers [1]. Note that this peak intensity ratio was cor- rected by the thickness of the wafer. Although ZnO and GaN are the wurtzite structure, direct bandgap, and have almost the same bandgap values, the difference in peak intensity of the gamma-ray induced photo emission observed in the present study is considered to be due to the difference in the light emitting mechanism between YL of GaN and GL of ZnO. YL of GaN has been proposed as a transition from a shallow donor to gallium vacancy (VGa) located at about 1.1 eV above the valence band [4]. Our previous study [5] reported that the low-dose gamma-ray irradiation of 160 kGy mainly induces N vacancies (VN) located at about 50 meV below the conduction band. Therefore, the gamma-ray induced YL observed in GaN is attributed to a shallow donor to VGa transition due to the excitation from valence band to conduction band by Compton electrons. On the other hand, GL in ZnO is the recombination of electrons in singly ionized oxygen vacancy (Vo^{+}) with photo-excited holes in valence band. However, it is suggested that a part of the electrons in Vo+ in ZnO are excited in the conduction band by the Compton electrons and Vo^{+} become the doubly ionized states (Vo^{++}), reducing their contribution to GL. As in the previous report [2], this situation is similar to the Vo^{+} signal observed in the electron paramagnetic resonance measurements of ZnO irradiated with the total gamma-ray dose of 170 KGy disappears with red LED illumination.

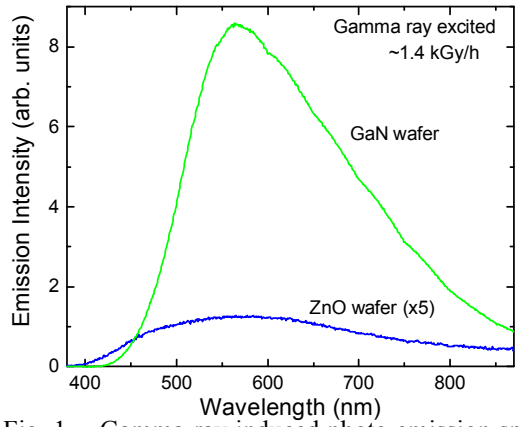


Fig. 1. Gamma-ray induced photo emission spectra from GaN and ZnO single crystal wafer.

Part of this research was published in Solid State Communications 336, 114413 (2021).

REFERENCES:

[1] T. Nakamura, T. Nishimura, K. Kuriyama, T. Nakamura, A. Kinomura, Appl. Phys. Lett. 118 (2021), 032106.
[2] J. Tashiro, Y. Torita, T. Nishimura, K. Kuriyama, K. Kushida, Q. Xu, A. Kinomura, Solid State Commun. 292 (2019) 24.
[3] L.E. Rehn, R.C. Birtcher, J. Nucl. Mater. 205 (1993) 31.
[4] J. Neugebauer J, C.G. Van de Walle, Appl. Phys. Lett. 69 (1996) 503.
[5] Y. Torita, N. Nishikata, K. Kuriyama, K. Kushida, A. Kinomura, Q. Xu, J. Phys.: Conf. Series 864 (2017), 012016.

PR3-5 Investigation of Free Volume in Diamond-like Carbon Films Deposited by Variouos Methods

K. Kanda, T. Mishima, F. Hori[1], A. Yabuuchi[2] and A. Kinomura[2]

Laboratory of Advanced Science and Technology for Industry, University of Hyogo
[1]Department of Materials Science, Osaka Prefecture University
[2]Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: As diamond-like carbon (DLC) has the lowest friction coefficient among various coating materials and its aggressiveness toward other materials is much less, its practical use have wide spread applications in, for instance, automobile parts, magnetic storage disks, implant parts, and food containers [1]. The film properties of DLC film is depended on its three kinds of structural factors, that is, sp^2/sp^3 ratio of carbon atom, hydrogen content, and free volume. The free volume in DLC film strongly related to the several physical properties of the DLC films, especially important ones such as hardness, Young's modulus, electrical conductivity, and gas barrier properties. In this study, the free volume of DLC films was discussed from the positron annihilation spectroscopy (PAS) study using a slow positron beam.

EXPERIMENTS: Eight kinds of DLC films were prepared. The following five methods were used for film deposition, ion plating, unbalanced magnetron spattering, plasma-enhanced chemical-vapor-deposition, DC sputtering, and filtered cathodic vacuum arc (FCVA) method. In FCVA method, four types of films were produced by varying the voltage. The measurements of Doppler broadening (DB) and positron annihilation lifetime spectroscopy (PALS) were carried out using a slow positron beam installed in the B-1 hole of KUR. Doppler broadening profiles of annihilation γ-rays were obtained using a Ge detector in the voltage range up to 30 kV. The Doppler broadening is characterized by the *S*- and *W*-parameters, corresponding to the annihilation with low and high momentum electrons, respectively. PALS was performed at an energy of 2 keV, corresponding to the DLC film on Si. The film density and the hardness were determined from X-ray reflectivity (XRR) measurements, and nanoindentation method, respectively.

RESULTS: The *W*-parameters were plotted as a function of the *S*-parameter in Fig. 1. The *W*-parameter of various DLC decreased linearly with increasing of the *S*-parameter. This indicated that the same types of positron trapping sites are present. In other words, different types of vacancies were not created with different deposition methods or under different film deposition conditions. In addition, the PAL and the *S*-parameter show very good correlation, except for the DLC film with specifically high hydrogen content.

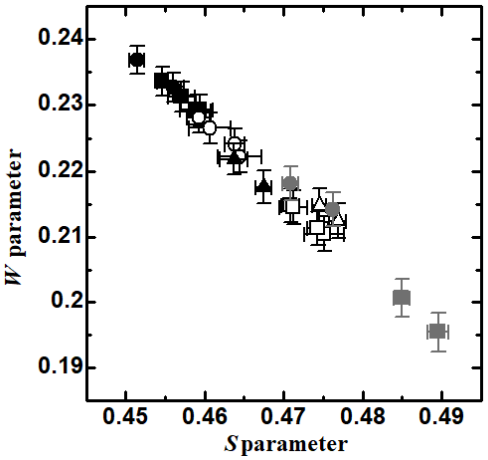


Fig. 1 The core annihilation parameter *W* versus the valence parameter *S*, in various DLC films.

Figure 2 shows the correlations between the *S*-parameters of various DLC films and the density and Martens hardness of DLC films. *S*-parameter shows good correlation with film density and the hardness. As the density and hardness decrease, the *S*-parameter increases, since the increase in *S*-parameter is considered to mean the increase in free volume. As well as, PAL increased with decreasing of the density and hardness. On the other hand, it was found that the *S*-parameter and PAL have no direct correlation to the hydrogen content, which was estimated rom the ERDA analysis, or the sp^2/sp^3 ratio of carbon in the DLC film, which was obtained from the NEXAFS measurements. This is because the magnitude of the *S*-parameter and PAL depends first of all on the size of the free volume, and the influence of the chemical environment around the free volume is a secondary factor.

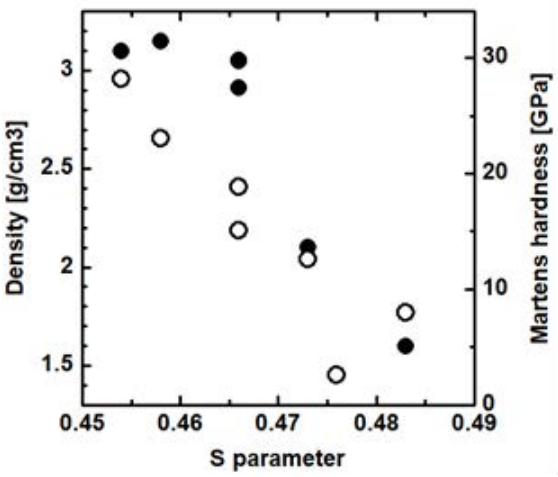


Fig. 2 Correlations between density, hardness and *S*-parameters of DLC films. ●: Density [g/cm^3], ○: Hardness [GPa]

REFERENCES:

[1] N. Ohtake *et al*., Materials **14** (2021) 315.

PR3-6 Positron annihilation spectroscopy on diamond-like carbon films

S. Nakao, X. Qu[1], A. Yabuuchi[1] and A. Kinomura[1]

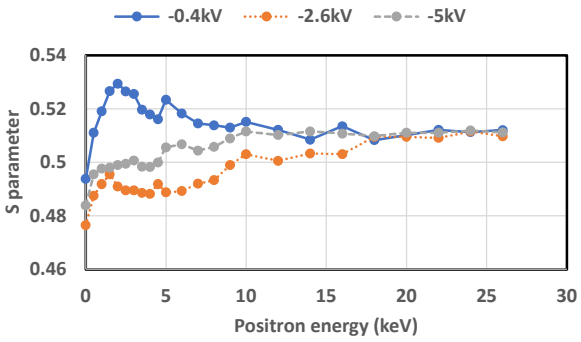
Innovative Functional Materials Research Institute, National Institute of Advanced Industrial Science and Technology
[1]Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: Diamond-like carbon (DLC) films have attracted much attention because of their excellent mechanical properties. However, the properties strongly depend on the microstructure of the films which is varied by the deposition conditions and methods. Recently, DLC or carbon films are categorized from type I to VI, which includes graphite-like carbon (GLC) and polymer-like carbon (PLC).
The thermal stability of the films is of importance for practical applications. However, the thermal stability is not always enough at high temperature. It is considered that the degradation of the properties should be caused by the changes of the microstructure at high temperature. The structural changes may be related to hydrogen (H) desorption and the creation of defects at high temperature. Many studies have been carried out on the thermal stability of DLC films. However, the principal phenomena, such as defect behavior, are not always clear. Therefore, to make clear the behavior of defects is necessary for every type of DLC films (type I to VI) because of different microstructure and hydrogen content. The positron annihilation spectroscopy (PAS) is one of the useful methods to clarify the defect behavior of materials. The aim of this study is to examine the relationship between the thermal stability and the behavior of defects in several types of DLC films by PAS measurement.
It is known that the thermal stability of DLC films may be improved by the incorporation of Si element into the amorphous network of the films (Si-DLC). However, the reason is not always clear. In this study, Si-DLC and Si-PLC films are prepared and annealed up to 800°C, and the samples are examined by PAS measurement.

EXPERIMENTS: Si-DLC and Si-PLC films were deposited on Si (100) substrates by bipolar-type plasma-based ion implantation and deposition (PBII) system. A mixture of trimethylsilane (TMS) and acetylene gases was used. Negative pulse voltage (V_n) was changed from -0.4 to -5 kV to change the structure from polymer-like to diamond-like in the films. The details on the PBII system were reported elsewhere [1].
Samples were annealed at 400°C and 800°C in vacuum by an infrared image furnace. In the PAS measurement, the S-parameter was obtained at different positron energies ranging from 0 to 30 keV. The S-parameters of single crystal diamond, Si wafer and highly oriented pyrolytic graphite (HOPG) were also measured as a reference.

RESULTS: Figure 1 shows the change in S-parameter obtained from the PAS spectra of the samples prepared at different V_n (a), and the samples after annealed (b). The sample of -0.4kV is categorized to Si-PLC and the others of -2.6 and -5kV are categorized to Si-DLC. The Si and H concentration was decreased with increasing V_n. The S-parameters of the references, diamond, Si and HOPG were ~0.48, ~0.51 and ~0.47, respectively. It is clearly seen in the Fig.1 that the S-parameters of ~0.51 at higher energies correspond to Si substrates. The S-parameters of the films should correspond to the low energy portion at least less than 5keV. The S-parameters of Si-PLC reaches ~0.53 which is higher than that of Si wafer. With increasing V_n, the parameters decrease to ~49, possibly due to densification by ion bombardment. Further increase of V_n may cause the increase of defects in the films so that the S-parameter slightly increases to ~0.5. On the other hand, thermal annealing causes the S-parameters decrease to ~0.51 in the sample of Si-PLC. It was noted that the S-parameter of PLC was like that of DLC and decreased from ~0.49 to ~0.475 after annealed at 800°C (not shown). These results suggest that Si incorporation may promote to increase porosity in the films and prevent structural changes due to H release by ion bombardment at high V_n or thermal annealing at high temperature.

(a)



(b)

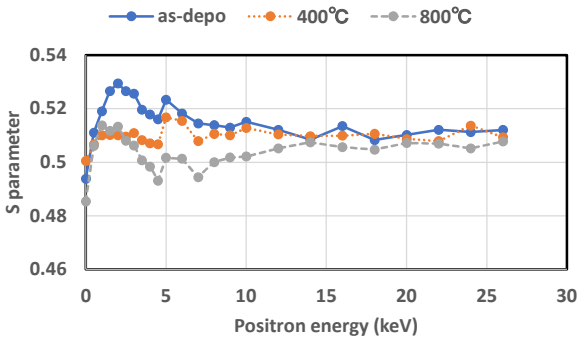


Fig.1. The change in S-parameter of samples at (a) different negative pulse voltage and (b) different annealing temperature.

REFERENCES:
[1] S. Miyagawa *et al.*, Surf. Coat. Technol., **156** (2002) 322-327.