I. Project Research

Project 12

PR12 Enhancement of research methods for material irradiation and defect analysis

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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, 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 facilities 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 techniques 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 subject (ARS) and individual co-researchers are listed below. Note that the titles of research subjects are based on individual reports.

ARS-1:
Study to improve transport and measurement performance of a slow positron beamline (A. Kinomura et al.)
ARS-2:
Electron-irradiation induced defects in W-Re (K. Inoue et al.)
ARS-3:
Change in the positron annihilation lifetime of electron-irradiated F82H by hydrogen charging (K. Sato et al.)
ARS-4:
The effect of gamma-ray irradiation on luminescence properties of collolidal Si nanocrystals (T. Nishimura 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:
Measurement of positron lifetimes of various diamond-like carbon thin films (K. Kanda et al.)
ARS-7
Positron annihilation spectroscopy on diamond-like carbon films (S. Nakao et al.)

RESULTS: In ARS-1, transport and measurement performance of the KUR slow positron system was evaluated with a positron beam during the KUR operation. The brightness enhancement system and positron lifetime measurement system were confirmed to be effective.

In ARS-2, electron-irradiation to introduce only a simple Frenkel pair to W or W-5%Re (in weight %) was performed. The effect of Re addition on the defect formation is investigated by the positron annihilation method. Positron lifetime spectra before and after elecron-irradiation were well fitted with one component both even after irradiation.

In ARS-3, the quantity of hydrogen atoms trapped at vacancy clusters in electron-irradiated F82H was evaluated by positron annihilation spectroscopy. The samples were soaked with liquid nitrogen within 5 min from the end of hydrogen charging. Isochronal annealing for 0.5 h was conducted every 25 K from 123 to 298 K. Subsequently, isothermal annealing was also conducted at room temperature (298 K).

In ARS-4, the effect of gamma-ray irradiation on luminescence properties of colloidal Si nanocrystals was investigated. The heavy dose irradiation of gamma-ray on the colloidal Si nanocrystals causes the decrease in photoluminescence intensity. A Compton effect on the Si core of nanocrystal is attributed to the photoluminescence quenching.

In ARS-5, irradiation techniques for study on corrosion resistance of fusion divertor materials to liquid metal during irradiation have been developed. Aluminum rich ferritic steel (Fe-18Cr-3.3Al-0.4Si) NTK04L in liquid Sn and FeCrAl-ODS in liquid Pb-Li were irradiated by KURNS-LINAC in 1st and 2nd experiments in this year. The validity of the developed specimen holders and measurement circuits was examined.

In ARS-6, free volume in the 4 kinds of DLC films was evaluated by the results of positron annihilation spectroscopy (PAS) and nano-indentation hardness. Positron lifetime decreases with increasing hardness. The relative S parameter also shows a tendency similar to a positron lifetime, but does not completely agree.

In ARS-7, several types of DLC and carbon films were also examined by PAS measurement for as-grown and thermally-annealed films. The results suggest that the structural changes, possibly caused by hydrogen desorption, may depend on the source gases and the films prepared by C_2H_2 should be less stable than those prepared by C_7H_8.

SUMMARY: Several new developments on irradiation (electron-beam and gamma-rays) and analytical techniques (beam and bulk positron measurements) for new materials have been continuously performed in the line of the objectives of this project. Such studies may enhance developments of new materials in various scientific fields.

PR12-1 Study to improve transport and measurement performance of a slow positron beamline

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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 applicable for practical use. Positron sources based on pair creation, in general, 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, brightness enhancement techniques 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: The brightness enhancement system of the KUR slow positron beam system has been evaluated in terms of the spot size and the beam intensity. A single-crystalline Ni thin film annealed in vacuum at 750 ^{o}C for 1h was used as a remoderator of the brightness enhancement system. The Ni remoderator film was cleaned by thermally excited hydrogen atoms after installation in vacuum to remove contamination during handling in air.

In addition to the detailed studies of last year, the performance of the brightness enhancement system was re-evaluated. In particular, transport of a brightness-enhanced beam to the downstream and efficiency of remoderator thin films were investigated again after careful treatments of the remoderator film and measurements of beam intensities.

RESULTS: The trajectories of the beam were optimized by adjusting voltages for the source components and currents for transport coils by observing images of phosphor screens on microchannel plates (MCP's). In particular, the excitation current of the focusing lens of the brightness enhancement system was optimized by observing the spot images on the MCP screen positioned at the focal point of the lens. The spot sizes at individual MCP screens were evaluated using photographs of the spot images taken by a digital single-lens reflex camera with a CMOS CCD (charge coupled device) image sensor. To avoid unnecessary data processing in the camera, a RAW-mode (a raw-data mode without data processing) was selected for this experiment. Linearity of used devices such as the MCP, the phosphor screen and the CCD was taken into account. Parameters of image acquisition were appropriately selected to keep the linearity of the combination of these three devices.

Figure 1 shows the images of the beam spots before and after the brightness enhancement. The distribution of the beam spot were different for horizontal and vertical directions. Furthermore, the positron source near the reactor core has a circular shape but the images of Fig. 1(a) was uneven (not circular). We believe that the original beam (i.e., circular beam) extracted from the source was cut several times by the walls of vacuum ducts during beam transportation. Regardless of these results, we evaluated spot size as a full-width at half-maximum (FWHM) value for horizontal and vertical directions.

Demagnification factors calculated from the spot image were close to 1/10. The efficiency of the remoderator in the case of an extraction energy of 6.5 keV was measured to be ~4% by gamma-ray intensities measured from the MCPs placed before and after the brightness enhancement system. As the beam loss at the acceleration mesh before the brightness enhancement was assumed to be 80%, the actual remoderation efficiency of the Ni film was estimated to be higher than the measured efficiency. The estimated efficiency value is acceptable but the contribution of high energy positrons (i.e., insufficiently remoderated positrons) should be taken into account for further discussion.

Finally, positron annihilation lifetime spectroscopy was examined by optimizing a positron pulsing and measurement systems. Trial measurements for Kapton and crystalline Si samples were successfully performed.

In summary, transport and measurement performance of the KUR slow positron system was evaluated with a positron beam during the KUR operation. The brightness enhancement system and positron lifetime measurement system were confirmed to be effective.

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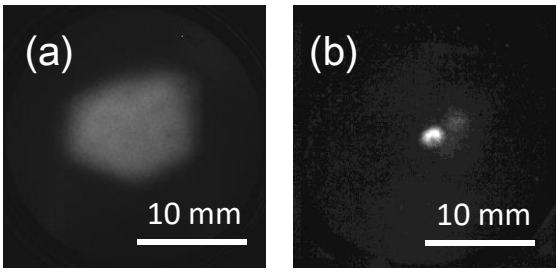

Fig. 1 Beam spot images before (a) and after (b) brightness enhancement.

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INTRODUCTION:

Tungsten (W) is a primary candidate material for the plasma-facing components (PFCs) due to its high melting point and high sputtering resistance to energetic particles. Furthermore, the very low solubility of hydrogen isotopes in W is a notable advantage in reducing tritium (T) retention during the operation of fusion reactors. 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 has 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.

EXPERIMENTS:

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

RESULTS:

Figure 1 shows results of positron lifetime measurement before and after electron-irradiation for pure W and W-5%Re. Calculated values of positron lifetime at W bulk, mono-vacancy in W and di-vacancy in W are also shown by dashed lines. In pure W, the average lifetime, τ_{ave}, was about 120 ps before electron-irradiation, which is close to the value in W bulk. After electron-irradiation, τ_{ave} was about 140 ps, showing positron trapping to vacancy-type defects induced by electron-irradiation. The lifetime spectrum after irradiation was analyzed with two components; the shorter component, τ_1, and the longer component, τ_2. τ_2 was 215 ps, suggesting positron trapping at mono-vacancies and/or di-vacancies.

In W-5% Re alloy, τ_{ave} before electron-irradiation was 158 ps, longer than that for pure W before electron-irradiation. This implies an existence of defects before irradiation. τ_{ave} after electron-irradiation was 162 ps, only 4 ps longer than that for W-5%Re before irradiation. Remarkable increase of τ_{ave} was not observed after irradiation. Different from the case of pure W, the lifetime spectrum was well fitted with one component both even after irradiation, and Positron trapping at mono-vacancy was not clearly observed. The possible candidate for positron trapping site for W-5%Re after irradiation could be dislocations in which positron lifetime value may be shorter than mono-vacancy. Other candidate could be vacancy-Re complexes, however, positron lifetime value at vacancy-Re complex might be almost same as at mono-vacancy in W because Re and W are the "neighborhood" in the periodic table. Further studies by chemical analysis of positron annihilation sites with coincidence Doppler broadening measurements are now in progress to discuss electron-irradiation induced defects in W-Re.

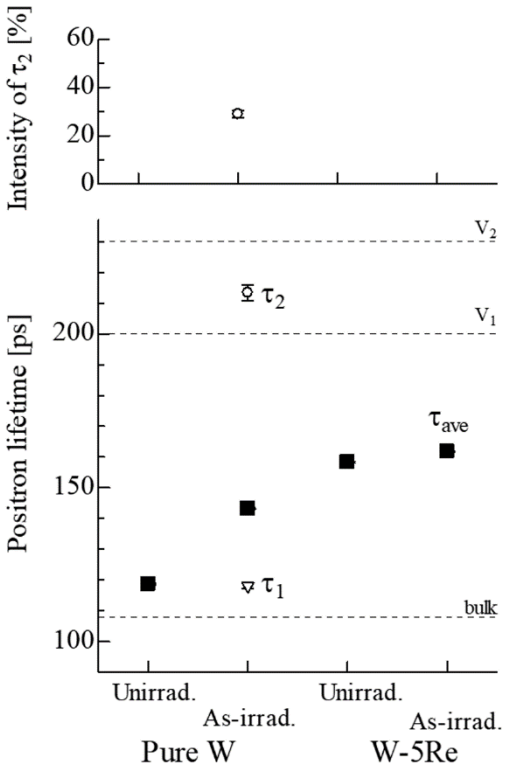

Fig. 1. Results of positron lifetime measurements for pure W and W-5Re alloy; before electron-irradiation (Unirrad.) and after electron-irradiation (As-irrad.).

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PR12-3 Change in the Positron Annihilation Lifetime of Electron-irradiated F82H by Hydrogen Charging

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INTRODUCTION: The structural materials of spallation neutron sources (SNS) cause more serious irradiation damage than fission reactors due to high-energy protons or spallation neutrons and the formation of extremely larger amount of gas atoms by nuclear transmutation [1, 2]. Therefore, irradiation resistance is required. Reduced activation ferritic/martensitic steel F82H, one of the can-didates for fusion reactor structural materials, has good thermal and mechanical properties [3]. Using this steel, many researchers have investigated the effect of He or H on its microstructural evolution [4−6]. The increase in hydrogen retention caused by the interaction with defects has an influence on the mechanical properties of structur-al materials [7, 8]. Vacancy-type defects are detected well by positron annihilation spectroscopy (PAS). Sato et al. determined the change in the positron annihilation life-time (PAL) through experiments and simulations [9]. Comparison and estimation of the number of hydrogen atoms trapped at single vacancies in electron-irradiated tungsten by PAS were performed [9]. In this study, the quantity of hydrogen atoms trapped at vacancy clusters in electron-irradiated F82H will be estimated by PAS.

EXPERIMENTS: Reduced activation ferritic/martensitic steel F82H IEA heat was used. Samples with diameters of 5 mm were cut from 0.4 mm-thick sheets using a wire electric discharge machine. Samples were irradiated with an 8 MeV electron linear accelerator from the Institute for Integrated Radiation and Nuclear Science, Kyoto University. The irradiation temperature was 333 ± 10 K, and the irradiation dose was 2.74×10^{27} /m^2 (1.75×10^{-4} dpa). Cathodic electrolysis charging was performed in an aqueous solution of 0.1 mol/L NaOH with the addition of 0.5 mass% NH_4SCN. The current density, temperature, and time for hydrogen charging were 50 A/m^2, 303 K, and 4 h, respectively. After hydrogen charging, the sample surface was mechanically polished using polishing paper #2400. Subsequently, samples were soaked with liquid nitrogen within 5 min from the end of hydrogen charging. The PAL measurements were conducted at a liquid nitrogen temperature of 77 K using a fast digital oscilloscope with a time resolution of 150 ps, i.e., full width at half maximum (FWHM) [11]. The PAL spectra were accumulated with a total count of approximately 3×10^6 and analysed using the PALSfit package [12]. Isochronal annealing for 0.5 h was conducted every 25 K from 123 to 298 K. Subsequently, isothermal annealing was also conducted at room temperature (298 K). To investigate the repeatability, the same samples used in the first experiment, which were left at room temperature for approximately 14 days, were subjected to the second hydrogen charging.

RESULTS: As dislocations, packet/block/lath boundaries, and precipitates exist in unirradiated F82H, a τ_1 of 140 ps, which denotes the PAL of dislocations [13], was fixed. After electron irradiation, a τ_2 of 254 ps was obtained. This PAL is almost the same as the calculated PAL of vacancy clusters composed of five vacancies (V_5). After hydrogen charging, τ_2 decreased to approximately 230 ps, and was constant until isochronal annealing at 273 K. After isochronal annealing at 298 K for 0.5 h, τ_2 started to increase during isothermal annealing for 1 h, 2 h, and 4 h, and was higher than the value before hydrogen charging (254 ps). When the isothermal annealing time reached 8 h, τ_2 decreased to the value before hydrogen charging. Almost the same trend of the change in PAL was observed in the second experiment. The cause of the increase in the PAL after annealing at 298 K from 0.5 to 4 h cannot be identified; therefore, it will be investigated in the near future.

From the theoretical estimation, the number of hydrogen atoms trapped at V_5 of 14.5 (θ = 0.805) is obtained. After the first and second hydrogen charging, the PAL decreases by 22 ps and 18 ps, respectively. Compared with the calculated result, each V_5 contains 4 hydrogen atoms (θ = 0.22). This value is significantly lower than the theoretical value. Analysis of the PAL spectra without fixing τ_1 of 140 ps was also performed, because it is better to obtain a stable PAL. The difference in the PAL between before hydrogen charging and after annealing at 148 K for 0.5 h was more than 50 ps. In this case, more than 14 hydrogen atoms can be trapped at each V_5. However, both τ_1 and τ_2 significantly change in each treatment. As F82H contains a variety of positron trapping sites such as dislocations, interfaces of precipitates, packet/block/lath boundaries, and vacancy clusters, identification of the positron trapping sites may be difficult in F82H. For future studies, samples with a different number of hydrogen atoms trapped at vacancy clusters will be prepared, and PAL spectra of F82H will be carefully analysed.

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PR12-4 The effect of gamma-ray irradiation on luminescence properties of collolidal Si nanocrystals

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INTRODUCTION: Colloidal crystalline silicon (Si) nanocrystals is known to exhibit a size tunable and efficient visible luminescence at room temperature due to quantum confinement effect. Because of its environmental friendliness and earth-abundancy, colloidal Si nanocrystals are a promising material for future light-emitting devices and biomedical applications. Various fabrication techniques for colloidal Si nanoparticles have been developed, such as wet-chemical synthesis and high-temperature thermal processing. Recently, we developed an efficient formation process of colloidal Si nanocrystals from porous Si, which is an interconnected wire-nanostructure assembly, as a raw material with low energy cost treatments. This process produces a large amount of colloidal nanocrystals per batch, and thus it allows us to utilize the Si nanocrystals in practical applications.

Optical properties of Si nanocrystals including luminescence properties are strongly affected by surface chemistry [1]. In particular, insufficient surface terminations causes the notable decrease in the luminescence efficiencies due to the formation of nonradiative centers i.e., dangling bonds. Thus, ambient condition is one of the most important key parameters to determine the luminescence efficiency. There are many reports on the effects of various environments on luminescence properties of Si nanocrystals. For example, it has been reported that a highly oxidant condition such as high humidity environment promotes inhomogeneous oxidation as well as removal of terminated spices on the Si nanocrystals and resultantly the decreases in luminescence intensity occurs. However, the effect of extreme conditions such as high level radiation environment on Si nanocrystals luminescence properties is not known.

In this work, we investigate the effect of gamma-ray irradiation on luminescence properties of colloidal Si nanocrystals. The heavy dose irradiation of gamma-ray on the colloidal Si nanocrystals causes the decrease in photoluminescence intensity. However, we find that, comparing with compound semiconductor nanocrystals such as CdSe, the decreasing effect is much weaker.

EXPERIMENTS: The porous Si used was prepared by a chemical etching of bulk Si. After the etching, porous layer was formed on the wafer surface, and then, samples were obtained. The formed sample exhibited a weak red photoluminescence. For preparing the colloidal Si nanoparticles, porous Si were firstly dispersed in an organic solvent with a quartz cuvette. Then, pulsed laser light at 266 or 532 nm from a Q-switched Nd:YAG laser (Continuum) was irradiated with a pulse duration of 5 ns and a repetition rate of 15 Hz. During laser irradiation, the porous Si dispersed in the organic solution were constantly stirred by a magnetic stirrer. After the pulsed laser irradiation of porous Si, the colloidal solution sample is obtained. Under UV illumination, the colloidal Si nanocrystal solution exhibits red luminescence.

For gamma ray irradiation experiments, we spin-coated the Si nanocrystals solution on the Si surface and the colloidal Si nanocrystal films were obtained. The prepared film samples were irradiated at room temperature with gamma-rays of 1.17 and 1.33 MeV from a cobalt-60 source of Institute of Integrated Radiation and Nuclear Science, Kyoto University. The dose rate of the irradiation was 1.771 KGy/h. Total gamma-ray dose was ~150 kGy.

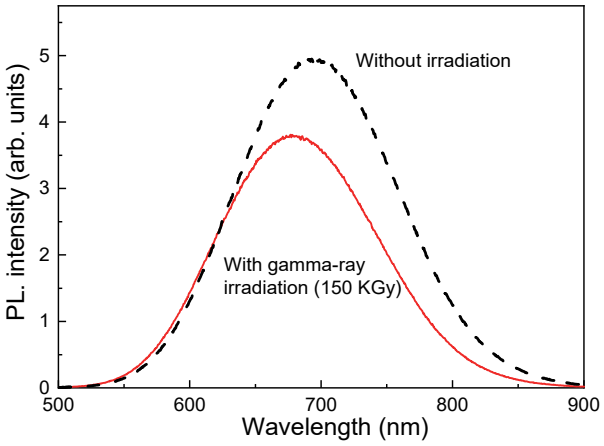

Fig. 1. PL spectra of colloidal Si nanocrystal films with and without gamma-ray irradiation.

RESULTS: Figure 1 shows PL spectra of colloidal Si nanocrystal films with and without gamma-ray irradiation. As shown in the figure, the heavy dose irradiation of gamma-ray on the colloidal Si nanocrystals causes the decrease in photoluminescence intensity. This may be due to the formation of defect centers formed by gamma-ray irradiation. However, the degree of the intensity decrease is much smaller than colloidal CdSe nanocrystals where the origin of the photoluminescence quenching is gamma-ray induced losses of surface ligands [2]. In our previous work, it was shown that Compton electrons emitted by the gamma-ray irradiation causes lattice defects of ZnO crystals [3], where the degree of the luminescence intensity change is trivial in spite of heavily dose. Thus, in the present case, such a Compton effect on the Si core of nanocrystal is attributed to the photoluminescence quenching.

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PR12-5 Irradiation technique for study on corrosion resistance of fusion divertor materials to liquid metal during irradiation

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INTRODUCTION:

Development of divertor material is one of the most important issues for future fusion reactor, where high thermal conductivity in severe neutron irradiation environment, sputtering resistance, and low radioactivity is required. Although development of SiC ceramics, tungsten, and its composite material is furthered, neither has resulted in the solution of this problem.

The liquid divertor is completely different approach from the conventional divertor material development, that is covering a surface of material with coolant liquid metal, and it can expect to moderate damage to the structure material. There is little study on the compatibility of liquid metal and structure material, and furthermore, compatibility study during irradiation is quite limited.

EXPERIMENTS and RESULTS:

In the previous year, it was planned to perform the corrosion experiment after an electron irradiation. However, it is impossible to avoid corrosion on the surface by underwater or in air irradiation. Therefore, tin (Sn) was sealed in a small irradiation container (30×34×4mm) manufactured by SUS316L stainless steel, and inside of the container, aluminum rich ferritic steel (Fe-18Cr-3.3Al-0.4Si) NTK04L with 100μm Al_2O_3 oxidization coating was enclosed to performed electron irradiation by KURUNS-LINAC that achieved the corrosion action inner side of the container under irradiation environment.

In this year, at the first MT, NTK04L specimen (pre oxidation 1000℃ 10h) was irradiated during 1.1×10^5 sec (32.5h) to a dose of 5.8×10^{19}e that corresponds to 2.3 mdpa (for Fe E_d=40keV) and also ODS sp-10 specimen (pre oxidation 1000 ℃ 10h) was irradiated during 1.1×10^5 sec (32.5h) 6.5×10^{19}e that corresponds to 2.6 mdpa. With this irradiation, rear heat sink was rather small to make a difference small between front side and rear side temperature. However, for the first specimen, temperature at the front-side was increased to 500℃ while at the rear-side was only 300℃. In the case of the second specimen, air blower was settled at the front side while it was settle rear side at the first specimen. With this treatment, temperature at the front side was same 500℃ but rear side was kept 400℃.

At the second MT, FeCrAl-ODS specimen was irradiated in Pb-Li liquid metal during 1.1×10^5 sec (32.5h) to a dose of 6.6×10^{19} e that correspond to 2.6 mdpa, and also JLF-1-SS430 specimen was irradiated in Pb-Li during 1.1×10^5 sec (32.5h) to a dose of 6.8×10^{19}e that corresponds to 2.7 mdpa.

In this irradiation, temperature measurement was failed because of failure of several AD8495 thermo-couple amplifier IC. Only rear-side temperature was measured and kept it to 370℃, but after the irradiation, some liquid metal was over spilled from the container.

To measure the electron current, the specimen holder was connected to current meter and not connected to ground directly and also thermo couple was not connected to ground to measure electron current. It is better to connect the thermocouple to ground with temperature measurement, and disconnect them when current measurement is performed.

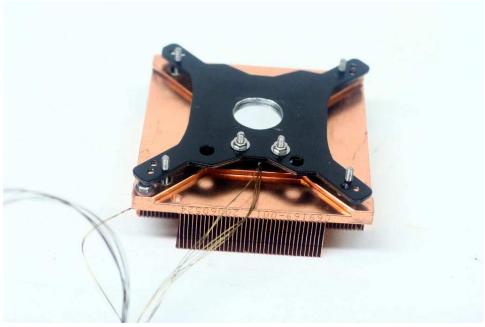

Fig.1. Cu heat sink and retention plate used for the electron irradiation. The irradiation container was placed between heat sink and the retention plate.

Fig. 2. In the second MT, over heat was assumed and some liquid metal was over spilled from the container.

PR12-6 Measurement of Positron Lifetimes of Various Diamond-like Carbon Thin Films

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INTRODUCTION: Diamond-like carbon (DLC) film, which is amorphous carbon film consisting of carbon and hydrogen, has several excellent properties, such as high mechanical hardness, chemical inertness, low frictional coefficient, and abrasion resistance [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 [2]. Free volume in the DLC film has been macroscopically evaluated as film density, but microscopic discussion on it has not been carried out yet. In the present study, free volume in the 4 kinds of DLC films, which were synthesized by various deposition methods and deposition conditions, was discussed on the results of positron annihilation spectroscopy (PAS). We also measured the nano-indentation hardness of these DLC films. Indentation hardness is expected to decrease as quantity and the size of the free volume increase.

EXPERIMENTS: We prepared 4 kinds of DLC films for the present study. The first DLC film was deposited by using a plasma-enhanced chemical vapor deposition (PE-CVD) method. On the present plasma condition, hydrogen-rich soft DLC film is expected to be deposited. The second DLC film was prepared by the ion plating (IP) method, which is very familiar to the industrial field as a hard protective coating. Last DLC films were is synthesized by filtered cathodic vacuum arc (FCVA) method. Two kinds of DLC films were deposited using this method with the different bias voltage, 100 and 400 V. All DLC films were deposited on Si wafer with the film thickness of several hundred nm. Indentation hardness of these DLC films was estimated by using a nano-indenter.
PAS measurement was performed at the slow positron beam system (B-1) at Kyoto University research Reactor (KUR). Doppler broadening profiles of annihilation γ-rays were obtained using a Ge detector for each positron energy. The-low momentum part of spectra was characterized by the line-shape *S* parameter, which is defined as the number of annihilation events over the range of 511 ± 0.80 keV. *S* parameters as a function of energy (S-E curves) were measured in the range of 0 - 30 keV. Positron annihilation lifetime spectroscopy (PALS) was performed at an energy of 2 keV, corresponding to the DLC film on Si. Figure 1 shows lifetime spectra for the DLC films formed by the FCVA method. A Kapton (polyimide) film was measured before and after measurements of the DLC samples as a control sample. Obtained lifetime spectra were analyzed by the PALSfit code assuming one-lifetime component.

RESULTS: Experimental results obtained from PAS measurements were summarized in Table with indentation hardness. Relative *S* parameter of each DLC film was obtained in comparison with that of and Si.

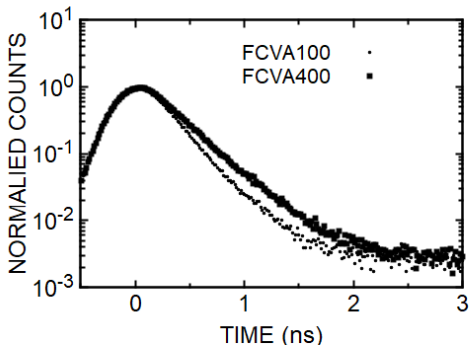

Fig. 1 Lifetime spectra for the DLC samples formed by the FCVA method with different bias voltage.

Table 1. positron lifetime and *S* parameter obtained from PAS measurements with nano-indentation hardness of each DLC films.

Deposition method	Bias voltage [V]	Positron lifetime [ns]	Relative S parameter	Indentation hardness [N/mm2]
PE-CVD		0.379	0.932	2488
IP		0.339	0.952	75960
FCVA	400	0.267	0.914	62303
FCVA	100	0.202	0.891	211795

The DLC film, which is synthesized by the FCVA method with the bias voltage of 100 V, has very high indentation hardness and its positron lifetime and relative *S* parameter are smaller than those of other DLC films. The DLC film deposited by the PE-CVD method, which has low hardness, has a large positron lifetime and relative *S* parameter. As described above, positron lifetime decreases with increasing hardness. The relative *S* parameter also shows a tendency similar to a positron lifetime, but does not completely agree. PAS techniques give information on voids consisting of the free volume. It should be noted that positron lifetimes reflect void sizes but *S* parameters reflect void densities in addition to void sizes. We think that the hydrogen in the DLC film influenced the results of the *S* parameter. We are planning to obtain the hydrogen content and the sp^2/sp^3 ratio of carbon atom in these films by measuring elastic recoil detection analysis (ERDA) and near-edge x-ray fine structure (NEXAFS), respectively.

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PR12-7 Positron annihilation spectroscopy on diamond-like carbon films

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INTRODUCTION: Diamond-like carbon (DLC) films have attracted much attention because of their excellent mechanical properties, such as high hardness, high wear resistance and low friction coefficients. 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 to use it at high temperature. It is considered that the changes of the microstructure at high temperature should be responsible for the degradation of the properties. The structural changes are related to H desorption and the behavior 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 thermal stability of DLC or carbon films, the examination on the defect behavior 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 in materials.
In a previous report [1, 2], the films of type I, III, IV, V and VI were examined by thermal desorption spectroscopy (TDS) measurement. From the results, it was found that hydrogen desorption clearly started around 400°C in the case of PLC (type VI) films. On the other hand, ta-C (type I) films did not change significantly until 800°C. The result, thus, suggested that defects may be created by hydrogen desorption and the behavior may play important role for the durability of the films. Several types of DLC and carbon films were also examined by PAS measurement for as-grown films [3]. It was found that the situation of the defect in the type III – VI films may be similar among as grown films except for ta-C (type I) films. In this study, thermal annealing and PAS measurement is carried out for a-C:H films (type IV) to make clear the effect of annealing temperature (hydrogen desorption).

EXPERIMENTS: Type IV (a-C:H) films were deposited using C_2H_2 and C_7H_8 source gases by plasma-based ion implantation (PBII) under the different conditions. Si wafer was used as substrate. The details on the PBII system were reported elsewhere [4]. The samples were heated at 400 and 800 °C for 1 h in vacuum by an infrared image furnace. The S-parameter was obtained at different positron energies ranging from 0 to 30 keV.

RESULTS: Figure 1 shows the change in S-parameter obtained from the PAS spectra of the samples prepared by (a) C_2H_2 and (b) C_7H_8 gases, which are annealed at different temperature. The sample prepared by C_2H_2 gas was peeled off after 800 °C annealing so that the one was not available for PAS measurement. In Fig. 1(a), the S-parameter of the as-grown film using C_2H_2 gas is around 0.50 and then that decreases to around 0.48 after annealed at 400 °C, which is close to that of graphite [3]. A similar trend is also observed in the sample prepared using C_7H_8 gas, as shown in Fig. 1(b). However, the changes of the S-parameter of sample (a) seems to be larger than those of sample (b) at 400 °C. These results suggest that the structural changes, possibly caused by hydrogen desorption, may depend on the source gases and the films prepared by C_2H_2 should be less stable than those prepared by C_7H_8. To make clear this point of view, more detail investigations are underway.

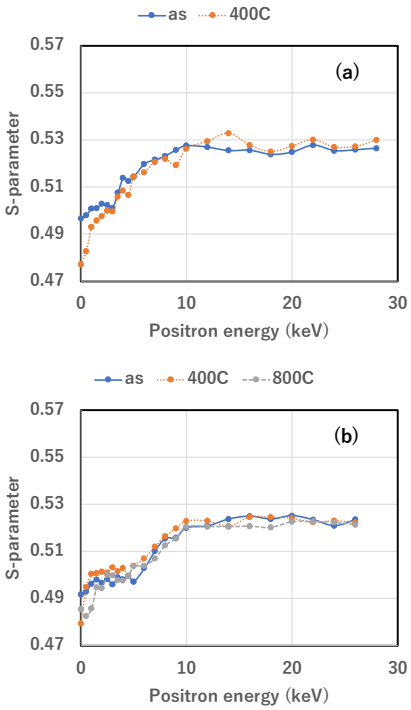

Fig.1. Changes in S-parameters of the samples after annealed at different temperature.

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