Structural analysis of carbon co-deposited layer in LHD

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The deposition layers that were formed at two different locations of LHD were analysed. Carbon is the major element within the layers. The structures in the deposited layers were analysed with XPS and Raman spectrometry. The sp2/sp3 hybridized orbital ratio of carbon was shown to be 0.8-0.95, which implies disordered carbon bonding. On the deposition layers, two-dimensional carbon bonding, as observed in the graphite structure, was not maintained because these structures were broken during the sputtering process. The ellipsometry analysis shows single C-H bonds in these deposition layers. These analytical results show a detailed amorphous structure in the deposited layers of LHD.

1. Introduction

Investigations of hydrogen isotope inventories in plasma-facing walls are important to control fuel recycling and in-vessel tritium inventories in fusion devices. However, the removal processes of retained hydrogen isotopes from the walls have not been optimized and are serious problems in ITER and DEMO. In particular, more hydrogen isotopes are retained in deposition layers than in bulk materials [1]. The retained hydrogen isotopes that originate from energetic hydrogen isotopes during plasma discharges and the molecular hydrogen isotopes have different depth profiles in the target materials [2-3]. In Tokamak devices, high-level tritium retentions are observed in the dome regions because molecular hydrogen isotopes are trapped in the deposition layers [3]. Thus, the trapped molecular hydrogen isotopes must also be investigated.

In ITER, plasma-facing materials are designed using tungsten and beryllium. In DEMO, some different materials may be considered for plasma-facing materials. Because carbon and metallic deposited layers have different hydrogen-trapping mechanisms, different analytical methods are required for the analysis. The characterizations of different deposition layers are particularly important to consider effective methods to remove hydrogen isotopes from the layers [4].

For metallic and mixed metal-carbon deposited layers, analytical methods are not optimized, and the understanding of hydrogen isotope trapping sites in the deposited layers is insufficient. For carbon deposited layers, some references presented optimized analytical methods [5] in which the relation between the amounts of retained hydrogen isotopes and the structure of the carbon layers, such as amorphous hydrogenated carbon (a:C-H), were investigated. However, for amorphous hydrogenated carbon, the parameters vary widely. In addition, it is difficult to clearly identify the C-H bonding. Hence, the analysis parameters are not sufficient for carbon deposited layers in fusion devices.

The present study shows the analysis results of deposited layers in LHD. In particular, the analytical results of a disordering of carbon bonding, sp2-sp3 hybridized orbitals and hydrocarbons are shown in carbon deposited layers.

2. Experimental

Two types of deposition layers were produced on stainless steel (SS) 316 target samples S2 and S3, which were set near the graphite divertor targets, as shown in Fig. 1, during an experimental campaign in LHD. Samples S2 and S3 faced different directions on the same holder. The minimum distance from the graphite divertor targets to the sample holder was approximately 20 cm. Sample S2 faced the divertor targets, and sample S3 faced in the opposite direction. Accordingly, sample S3 did not directly see the divertor targets. S2 and S3 had identical neutral gas pressures and temperatures.

The thicknesses and compositions of the deposited

layers were measured using Auger electron spectroscopy (AES). In AES, Ar^+ ions with an energy of 3 keV were set for sputtering. The amounts of retained hydrogen were measured using thermal desorption spectrometry (TDS). The target samples were heated from room temperature to 1273 K at a rate of 0.5 K/s and maintained at 1273 K for 15 min [6]. The desorbed gasses from the heated target samples were measured using quadrupole mass spectrometry (QMS).

The sp2-sp3 hybridized orbitals of carbon on the deposition layers were measured using X-ray photoelectron spectroscopy (XPS). A Mg X-ray source of 400 W and a spot size of 800 μm were used. The background intensities of these narrow profiles were removed using the Shirley method [7]. A peak binding energy of C1s was calibrated using a highly ordered pyrolytic graphite (HOPG) target. An argon ion gun was used to etch the target samples and analyse the depth profiles of the binding energies.

Raman spectra were measured (800 ~ 2000 cm^{-1}) using an Ar laser. The carbon deposition layers show a broad G peak (at ~1570 cm^{-1}), a D peak (at ~1350 cm^{-1}) and a continuous photo luminescence (PL) background [8]. Using a fitting analysis, the G and D peaks were separated, and the ratio of the two peak intensities of the G and D peaks and the full width at half maximum (FWHM) of the G peak were obtained.

The optical characteristics, which are connected to hydrocarbon bonding in deposited layers, were measured using ellipsometry. The commercial ellipsometer VASE (variable angle spectroscopic ellipsometer) from J. A. Woollam Inc. was used. The ellipsometer has a measurement range of 193-2000 nm, and the angle of incidence can be varied between 15 and 90°. The linearly polarized incident light beam was reflected by a sample, and elliptically polarized light was detected by a

photodiode. The response of the sample to the polarized light was measured as two ellipsometric angles: Ψ and Δ. After the analyses using these parameters, two parameters were obtained: refractive index (n) and extinction coefficient (k) [9].

3. Results and Discussion

According to the AES analysis, the thickness and composition of the deposition layer are 382 nm (80 %C and 15 % Fe) and 22 nm (60 %C, 25 %Fe and 5 %B) for samples S2 and S3, respectively. The amounts of retained hydrogen in the deposition layers are 1.03×10^{22} mol/m^2 and 1.10×10^{21} mol/m^2 for S2 and S3, respectively [4]. Hydrogen was mainly trapped in the deposition layers during the main plasma discharges and glow discharges in LHD. Because carbon is the major element of the deposition layers in the two samples, most hydrogen trapping sites are assumed to be carbon in the layers. The estimated hydrogen-carbon (H/C) ratio in the S2 and S3 layers are 0.23 and 0.55, respectively.

A comparison of the H/C ratio and retained hydrogen in the S2 and S3 samples shows that S3 has more hydrogen per carbon atom than S2.

The sp2-sp3 hybridized orbitals of carbon in the deposition layers were measured using XPS. A fitting analysis for the separation of sp2 and sp3 carbons is performed as shown in Fig. 2. A peak due to an sp2 carbon was observed at 285.59 eV using the HOPG target, and a peak due to an sp3 carbon was observed with a shifted binding energy from sp2 in Ref. 10. An sp2 satellite was estimated to be negligible and a carbon-dioxide bond is observed on sample S3. The XPS depth profiling shows weak variation of the sp2/sp3 ratio with depths for both S2 and S3: 0.95-0.8 for S2 and 0.9-0.8 for S3.
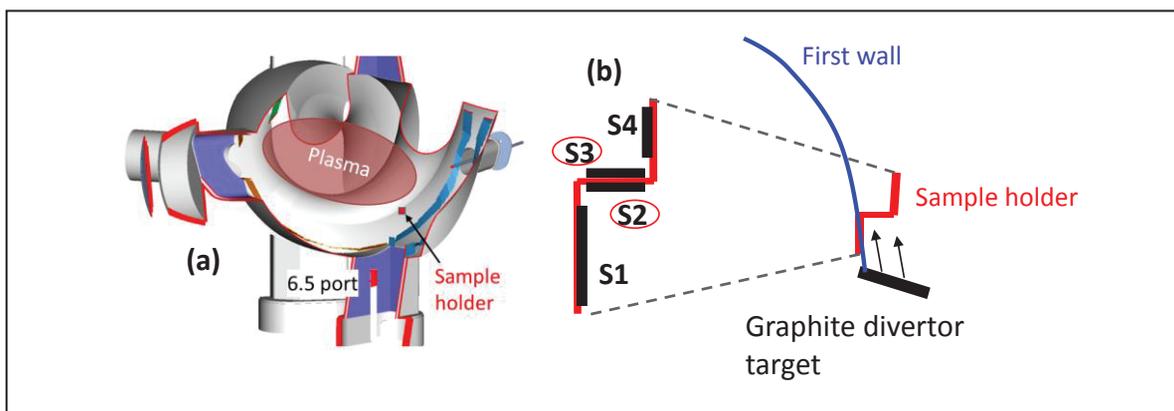
Figure 1. Setups of the sample holder and their location in LHD. (a) The sample holder was installed near the 6.5 port section. (b) The holder has two facings, the sample S2 facing to graphite divertor target and sample S3 facing to the opposite direction of sample S2.

In the field of plasma processing to produce diamond-like carbon (DLC), abundant data collections and analyses are performed [5]. The H/C and sp2/sp3 ratios for S2 and S3 were plotted in a ternary phase diagram of bonding in amorphous carbon-hydrogen alloys [12], and the type of amorphous carbon in the two samples was estimated. A hard type a-C:H was suggested as the type of hydrogenated carbon layer in LHD.

Disordered carbon-carbon bonds were measured using Raman spectroscopy. Raw data for the G- and D-bands were analysed, and the intensity ratio of the two
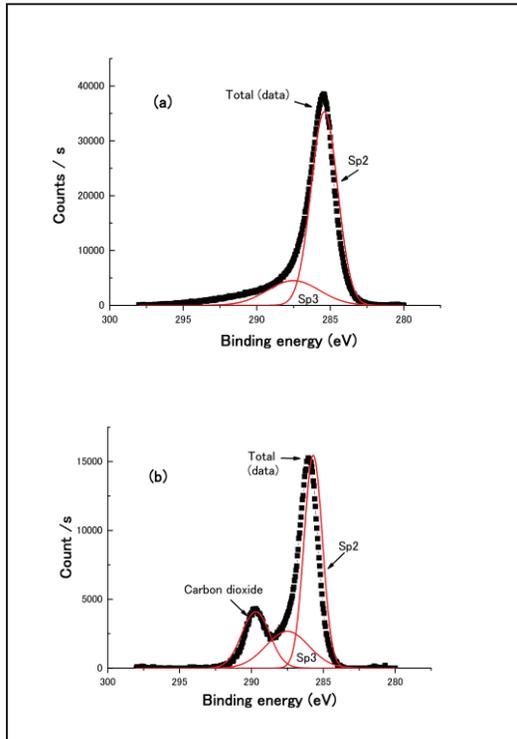
Figure 2. Narrow profile of C1s peak by XPS at (a) a depth of 31.8nm on sample S2 and (b) a depth of 4.5 nm on sample S3. A fitting analysis for the separation of sp2 and sp3 carbons is performed.
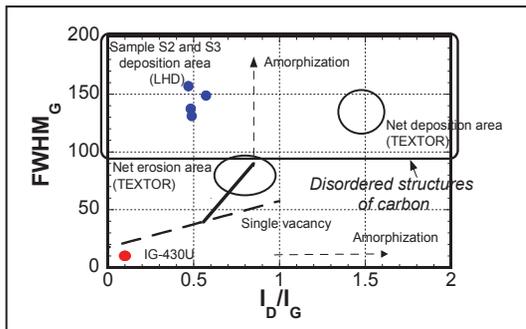
Figure 3. Analytical data of Raman spectroscopy for deposition layers on S2 and S3 samples of LHD (this work), IG-430U graphite target (this work) and deposition and erosion areas on graphite limiter of TEXTOR [11].

peaks and the full width at half maximum (FWHM) of the G peak are shown in Fig. 3. In Ref. 11, the same parameters of the net erosion and net deposition areas in TEXTOR were reported and are plotted in the same figure. For isotropic graphite (IG-430U), I_D/I_G is approximately 0.1 because a clear graphite structure near the G-band is observed. The FWHM of G-band is approximately 10 for this material. The FWHM of the G-band is related to the sp2 hybrid orbit as a graphite structure on a two-dimensional plane, and the high FWHM of the G-band indicates highly disordered carbon-carbon bonds. For the deposition layers on the S2 and S3 samples of LHD and the graphite limiter of TEXTOR, the observed FWHMs of the G-band are 120-160.

In general, graphite structures are broken because of the erosion-deposition processes, and it is difficult to recover this structure on deposited layers. Hence, deposition layers in LHD and TEXTOR show similar disordered carbon-carbon bonds.

The I_D/I_G ratio is inversely proportional to the crystal size of carbon, which was measured using X-ray diffraction [13]. For carbon deposited layers in fusion devices, the I_D/I_G ratios disperse, as shown in Fig. 3. Hence, the I_D/I_G ratios do not show the characteristics of the deposition layers in fusion devices.

Figure 4 shows the refractive index that was measured using ellipsometry. By comparing the data for LHD deposition layers and known materials, the types of C-H bonds were determined. Four targets were used as
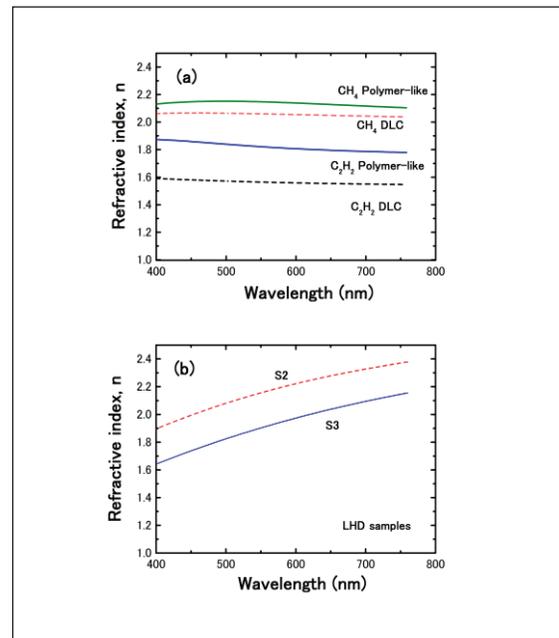
Figure 4. Refractive index measured by the the ellipsometry analysis (a) for reference data using known materials, (b) for LHD samples, S2 and S3.

known materials, as shown in Fig. 4 (a): CH4-polymer-like, CH4-DLC, C2H2-polymer-like and C2H2-DLC. The three targets methane (C≡H4)-polymer-like, methane DLC and acetylene (H-C≡C-H)-polymer-like are in the same parameter range of refractive indices as those for S2 and S3. The common characteristic of CH4-DLC, C2H2-DLC and C2H2-polymer-like is a single C-H bond. Thus, the major type of bonding in the carbon deposited layers of S2 and S3 may be single C-H.

4. Summary

The relations of retained hydrogen and analytical parameters were investigated for the deposition layers at two positions in LHD: facing and not facing the divertor.

Similar carbon characteristics were shown for the two deposition layers. The obtained sp2/sp3 hybridized orbital ratio of carbon and H/C were 0.8-0.95 and 0.2-0.5, respectively, for the two layers. From the relationship between sp2/sp3 and H/C and according to the database for DLC, a hard type a-C:H is expected for the type of carbon bonding in the two deposition layers.

Raman spectroscopy shows disordered carbon bonding. On the deposition layers, two-dimensional carbon bonding, such as that seen in the graphite structure, were not maintained because these structures were broken during the sputtering process on graphite targets. Thus, carbon deposited layers show higher parameters of $FWHM_G$, and similar types of disordered carbon bonds are shown in different locations.

Based on the ellipsometry analysis, C-H bonds in the carbon deposited layers were suggested. The analysed data for the deposition layers are in the same parameter range of CH4 polymer-like, CH4 DLC and C2H2 polymer-like structures, which contain single C-H bonds.

These analytical results show a detailed amorphous structure in the deposited layers of LHD.

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