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Journal of Nuclear Materials 258–263 (1998) 1087–1091

journal of nuclear materials

Retention and re-emission of deuterium implanted into tungsten monocarbide

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Abstract

The retention of deuterium in tungsten monocarbide on graphite, implanted with 5 keV D_2^+ ion beams up to saturation at room temperature and the re-emission of deuterium from tungsten monocarbide by post thermal annealings have been studied by means of the elastic recoil detection (ERD) technique. It is found that the steady state concentration of retained deuterium is 1.7×10^{22} cm^{-3} at room temperature, which decreases to 1.4×10^{22} cm^{-3} due to spontaneous re-emission in 5 h of terminating the implantation. It is also found on isothermal annealing at temperatures of 70°C, 100°C, 150°C, 200°C and 250°C that the concentration of retained deuterium decreases rapidly in the beginning and hereafter very gradually with increasing annealing time. The re-emission profiles have been analysed taking into account thermal detrapping (Σ_d), retrapping (Σ_T), local molecular recombination (K_1) between movable deuterium atoms. It is determined that the activation energy of the effective molecular recombination rate constant $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$ is 0.47 eV, where C_0 is the trap density and that the activation energy of the thermal detrapping rate constant Σ_d is 0.20 eV.

1. Introduction

Carbon materials have been extensively used in magnetically confined fusion devices because of their excellent thermal properties such as high thermal shock resistance and high thermal conductivity. Their use has provided significant performance in heating and confinement of a thermonuclear plasma. However, they have some drawbacks: such as enhanced erosion due to chemical sputtering [1–4] and radiation-enhanced sublimation [4–6]. In addition the concentration of hydrogen isotopes retained in plasma facing components is extremely high so that a large amount of them [7,8], emitted by the temperature rise and particle bombardment during the long term discharge, may not only cool down the plasma temperature but also induce a change of D/T ratio in the main plasma [9,10].

On the other hand, refractory metal carbides have a desired property of low sputtering yield [11]. There is a concern that the sputtering of high Z metal induces radiative cooling of hot core plasma, but TiC and WC coated on graphite have shown that the sputtering of metals is suppressed at high temperatures due to self-sustaining coverage of the surface with segregated carbon layer from graphite substrate [12,13]. High Z metal and carbon are expected to be used simultaneously as the divertor plate and the first wall armor in future fusion devices, respectively. The redeposition of each sputtered materials at temperatures above 1000°C modifies the surface layers into the metal carbides with each other for long term operation. Nevertheless, data on hydrogen in high Z metal carbides are hardly available [14]. Therefore, it is quite important to investigate hydrogen behavior in refractory metal-carbon composite materials.

In this paper, we report the experimental results on retention and re-emission of deuterium implanted into WC coated graphite with 5 keV D_2^+ ion beam which have been measured by means of the ERD technique. The experimental data for the carbide are compared with those for graphite.

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0022-3115/98/$19.00
PII: S0022-3115(98)00279-7

2. Experimental

Isotropic graphite plates (IG-110U) of $0.5 \times 5 \times 35$ mm^3 in sizes were used as a substrate of the specimen. The surface of the graphite plate was polished with fine diamond paste on which a W-film of 400 nm in thickness was deposited by electron beam heating. The WC-covered graphite specimen was prepared by direct current heating at 1400°C for 30 min. The specimen was characterized by means of the Rutherford backscattering spectroscopy (RBS) and an X-Ray diffraction (XRD) technique. It was found that the average atomic composition of WC by RBS was $C/W = 0.96 \pm 0.04$ and the lattice constants for hexagonal lattice were also $a_0 = 2.93 \pm 0.01$ Å and $b_0 = 2.85 \pm 0.02$ Å. Since the WC film was polycrystalline and the XRD analysis showed graphite peaks, some fractions of carbon were expected to exist in grain boundaries of the WC film.

In order to remove residual hydrogen, the specimen was preheated at 1000°C for 10 min before deuterium implantations. The implantation into the WC film was done with 5 keV D_2^+ ion beams up to saturation at room temperature and at a flux of 2.4×10^{13} cm^{-2} s^{-1}. The concentration of deuterium retained in WC was measured by means of the ERD technique [15], in which 1.7 MeV He^+ ion beam impinges on the WC surface at the angle of 85° to the surface normal and recoiled deuterium ions were also detected at the forward angle of 82° to the surface normal. An irradiation fluence of the probing He^+ ions for the ERD measurement was monitored by means of the RBS technique.

3. Results

First of all, deuterium retention in the $WC_{0.96}$ covered graphite specimen irradiated with 5 keV D_2^+ ions was measured. The total counts of retained number of D obtained from integral of the ERD spectrum are shown as a function of irradiation time in Fig. 1. It is seen from Fig. 1 that the retained number of D increases rapidly at an early stage of the irradiation and then saturates at a level, which was estimated to be 1.7×10^{22} cm^{-3}. And the value decreases to 1.4×10^{22} cm^{-3} in 5 h of terminating the irradiation, which corresponds to the saturation concentration of retained D.

The retained number of D in the specimen after isochronal annealings for 10 min is shown as a function of temperature in Fig. 2, where the vertical axis represents the retained number of D normalized by the saturation concentration. From Fig. 2, the re-emission of D is seen to take place at two stages. It is regarded that a large amount of D is re-emitted from the $WC_{0.96}$ layer at lower temperatures and a small amount of the remains is re-emitted from the carbons in grain boundaries at higher temperatures. The result is very similar to that obtained by Wang et al. [14].

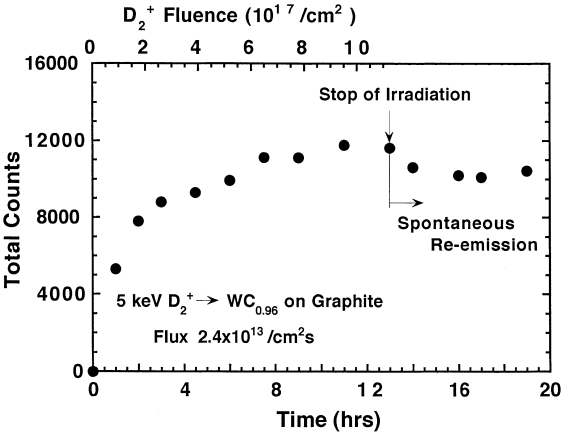

Fig. 1. Time variation of the number of D retained in a WC layer both during irradiation with 5 keV D_2^+ ions and after terminating the irradiation at room temperature.

Isothermal re-emissions were also measured at temperatures of 70°C, 100°C, 150°C, 200°C and 250°C. Typical ERD spectra of D obtained for the specimen as-implanted and annealed at 200°C for 10 and 300 min are shown in Fig. 3, where the ERD spectrum for graphite implanted up to saturation is shown for comparison. It is seen from Fig. 3 that the concentrations of D atoms retained decreases almost uniformly over the whole depth. The integrated numbers of retained D at different temperatures are shown as a function of the annealing time in Fig. 4, where the vertical axis represents the values normalized by the as-implanted one. It is clearly seen from Fig. 4 that the deuterium concentrations decrease rapidly in the beginning of annealing and hereafter decrease very gradually as the time increases. The analysis of the re-emission kinetics is described in Section 4.

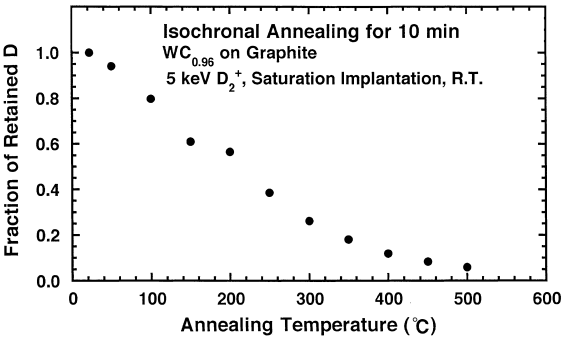

Fig. 2. Deuterium retention in a WC layer, implanted up to saturation at room temperature, after isochronal annealings for 10 min.

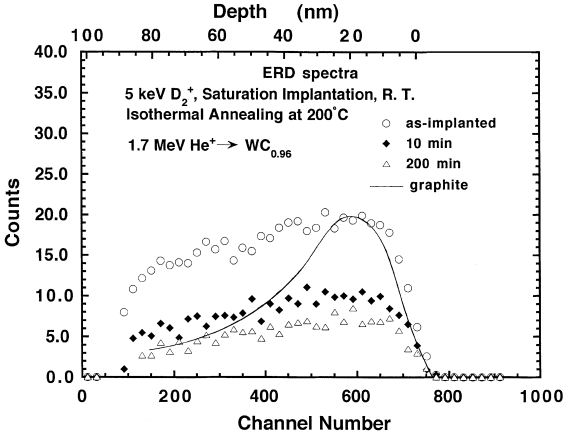

Fig. 3. Typical ERD spectra of D recoiled from a WC layer, implanted with 5 keV D_2^+ ions up to saturation at room temperature (○) and annealed at 200°C for 10 min (♦) and 200 min (△). Solid line represents the ERD spectrum from graphite shwon for comparison.

4. Discussions

The decay curves of deuterium concentration due to the isothermal re-emission in Fig. 4 indicate that the concentration decreases rapidly in the beginning of the annealing and hereafter gradually with time. The initial rapid decay is ascribed to no retrapping of thermally detrapped deuterium due to no existence of available trap sites in the WC layers because of saturation implantation. The late slow decay is attributed to strong retrapping of thermally detrapped deuterium into vacant trap sites produced by the initial decay. Therefore, the decay curves should be analyzed by solving the mass balance equations governing the time evolution of the concentrations of activated (free) and trapped deuterium

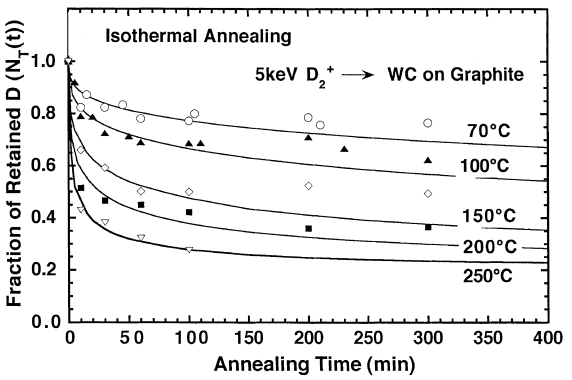

Fig. 4. Deuterium retention in a WC layer, implanted up to saturation at room temperature, during isothermal annealing at temperatures of 70°C, 100°C, 150°C, 200°C, 250°C. The solid lines represent the best fitting curves calculated using Eq. (3).

which take into account the following elementary processes: thermal detrapping, retrapping and local molecular recombination between activated species leading to the re-emission. The mass balance equations are described in the following forms:

$$\frac{dN(t)}{dt} = \Sigma_d N_T(t) - \Sigma_T N(t)(C_0 - N_T(t)n_0) - 2K_1 N^2(t)n_0, \quad (1)$$

$$\frac{dN_T(t)}{dt} = -\Sigma_d N_T(t) + \Sigma_T N(t)(C_0 - N_T(t)n_0), \quad (2)$$

where $N(t)$ and $N_T(t)$ are the average concentrations of activated and trapped deuterium atoms normalized by the initial implantation concentration n_0, respectively, Σ_d is the thermal detrapping rate constant, Σ_T is the trapping rate constant, K_1 is the local molecular recombination rate constant between activated species, and C_0 is the trap density. The assumption of local molecular recombination is based on the fact that the decay of retained deuterium takes place uniformly over the whole depth of the $WC_{0.96}$ film. The average concentrations were also taken into account, on the basis of the fact that the depth distribution of retained deuterium is uniform, as seen from Fig. 3. The decay kinetics of deuterium is expressed in the following equation as a solution of the mass balance equations [16]:

$$\frac{C_0}{n_0}\left(1 - \frac{1}{N_T(t)}\right) - 2\ln N_T(t) + \frac{n_0}{C_0}(N_T(t) - 1) = -2\frac{K_1}{C_0}\left(\frac{\Sigma_d}{\Sigma_T}\right)^2 t. \quad (3)$$

In order to obtain the rate constants Σ_d and $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$, Eq. (3) was fitted to the experimental data in Fig. 4. The thermal detrapping rate constants Σ_d determined from the slope of the initial decay of the curves, which is produced by the thermal detrapping-limited process because of no available trapping sites, are shown as a function of $1000/T$ (K) in Fig. 5. The activation energy of Σ_d is estimated to be 0.20 eV, which is lower by a factor of 3 than that for graphite [17]. The values of $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$ were determined by assuming that some fraction of deuterium atoms are retained in carbon, which would be segregated in grain boundaries of $WC_{0.96}$ crystallites. The best fitting was achieved so that the values of the left-hand side of Eq. (3) calculated by substitution of the experimental data in Fig. 4 into $N_T(t)$ of $N'_T(t)$ and the retained fraction in carbons as fitting parameter were proportional to annealing time, as shown in Fig. 6. For fitting, it was assumed that $n_0/C_0 = 1$, since the initial deuterium concentration was at a saturation level. It was found, as expressed by a relation in Fig. 6, that 20% of the total retained deuterium, namely 2.8×10^{21} cm^{-3}, were trapped in carbons segregated in the boundaries. This fact indicates that the

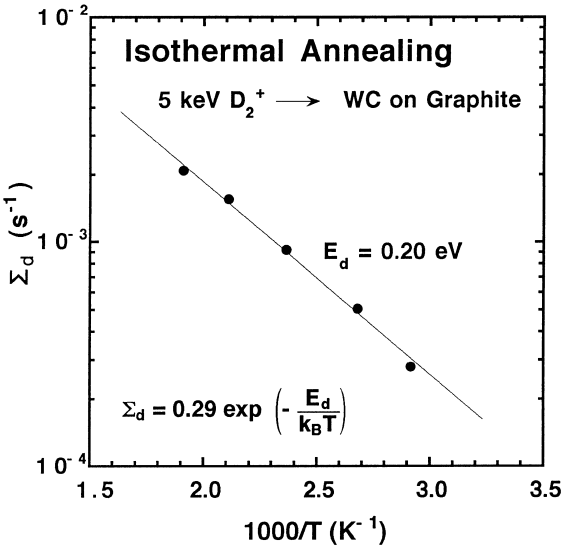

Fig. 5. Arrhenius plot of the experimental values of Σ_d vs. $1000/T$.

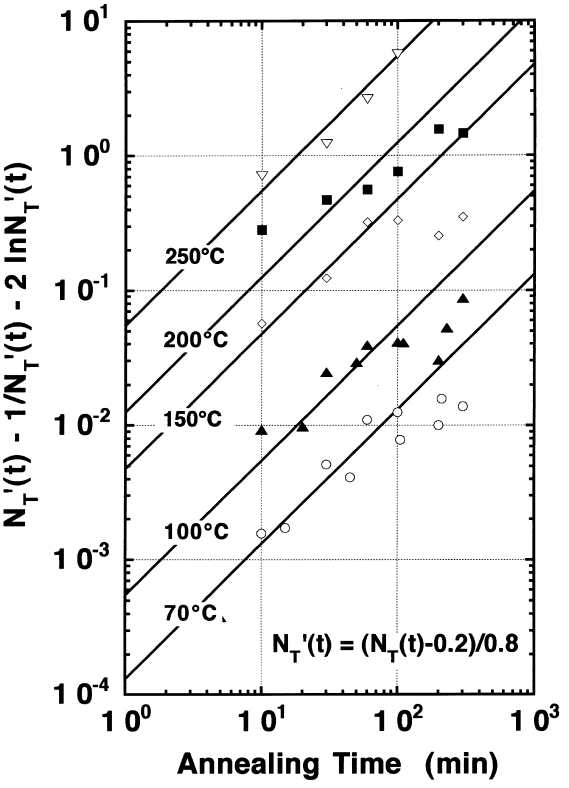

Fig. 6. A log–log plot of $N'_T(t) - 1/N'_T(t) - 2\ln N'_T(t)$ vs. annealing time best-fitted by substituting the experimental re-emission data in Fig. 4 into $N_T(t)$ of $N'_T(t)$. 20% of deuterium trapped in the specimen were assumed to be trapped in carbons segregated in grain boundaries of WC crystallites.

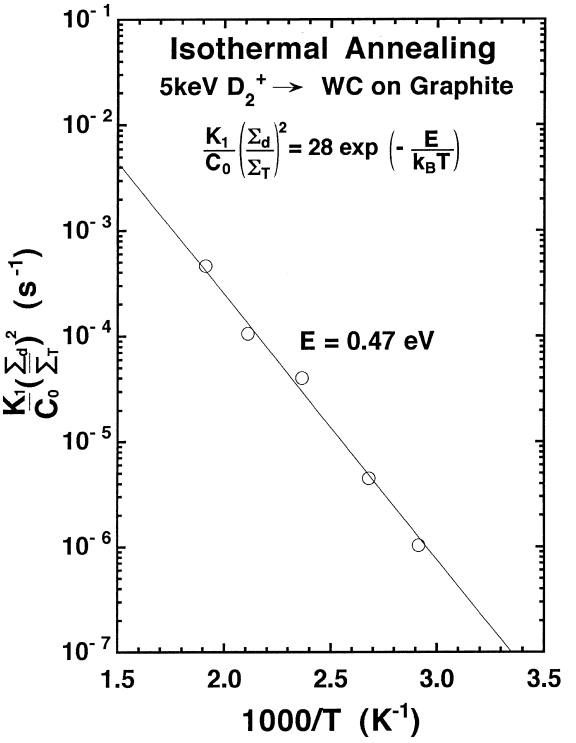

Fig. 7. Arrhenius plot of the experimental values of the effective recombination rate constant $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$ vs. $1000/T$.

effective volume of carbons in the grain boundaries is several % of the WC layer, which might include carbon-interstitial clusters produced by the deuterium ion implantation. It is seen from Fig. 4 that the best fitting curves of solid lines reproduces fairly well the experimental deuterium retention except the long annealing time.

The values of $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$ regarded as the effective local recombination rate constant, are shown as a function of $1000/T$ in Fig. 7. The activation energies of $(K_1/C_0)(\Sigma_d/\Sigma_T)^2$ were estimated to be 0.47 eV. This value is considerably smaller than that (1.2 eV) for graphite [17].

In conclusions, these results indicate that the re-emission of deuterium from the WC layer takes place much more preferably than that from graphite. This fact is ascribed to much faster diffusion of deuterium in the WC layer than that in graphite, as seen in Fig. 3.

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