Irradiation Effects on the Retention of Hydrogen in Al_2O_3 *

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Substantial defects are produced in Al_2O_3 by 4 MeV Au ion irradiation with a fluence of 4.4×10^{15} cm^{-2}. Rutherford backscattering spectrometry/channeling and cross-sectional transmission electron microscopy methods are used to investigate the irradiation damage. The 190 keV H ions with a fluence of 1×10^{17} cm^{-2} are used for implanting pristine and Au ion irradiated Al_2O_3 to explore the irradiation damage effects on the hydrogen retention in Al_2O_3. The time-of-flight secondary ion mass spectrometry method is used to obtain the single hydrogen depth profile and ions mass spectra (IMS), in which we find that implanted hydrogens interacted with defects produced by Au ion irradiation. In IMS, we also obtain the hydrogen retention at a certain depth. Comparing the hydrogen retention in different Al_2O_3 samples, it is concluded that the irradiation damage improves the tritium permeation resistance property of Al_2O_3 under given conditions. This result means that Al_2O_3 may strengthen its property of reducing tritium permeation under the harsh irradiation environment in fusion reactors.

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Tritium permeation barrier (TPB) is a major scientific issue in fusion reactors. Tritium leakage from fusion plants will give rise to not only loss of tritium fuel, but also nuclear contamination of the external environment. TPB can effectively reduce the leakage of tritium to the outer structural material, which ensures the safe operation of fusion reactors. A great amount of research has been carried out to investigate the tritium permeation resistance property (TPRP) of Al_2O_3, proving that it is a promising material as TPB in fusion reactors. Al_2O_3 has a great tritium permeation reduction factor (PRF), and its hydrogen permeability is extraordinarily low.[1–3] It is well known that in fusion reactors, neutron irradiation damage will influence the tritium permeation through Al_2O_3, which is primarily investigated in the present work. However, neutron irradiation experiment is limited for the reasons of long time and high cost. Ion irradiation can be a convenient way to simulate the neutron irradiation, but the optimum ions need to be explored.[4–6] Much research has been carried out to study the irradiation damage in Al_2O_3 in recent decades.[7–11] However, the interaction between irradiation defects and hydrogen has not been researched thoroughly. Recently, Zhang *et al.* have experimentally proved the interaction between hydrogen and vacancy defects in Al_2O_3. What is more, they have theoretically predicted that H-related vacancy defects play an important role in the low H transport in TPB.[12–14] Some research has been carried out to investigate how electron irradiation influences the hydrogen retention in Al_2O_3,[15] showing that ionizing irradiation enhances the interaction between hydrogen isotopes and Al_2O_3.

In this Letter, it is aimed to further explore the interaction between hydrogen and irradiation defects as well as the effects of the interaction on the transport of hydrogen in Al_2O_3. Au ions have been chosen to produce substantial irradiation damage in Al_2O_3, followed by H ion implantation. As a comparison, the other Al_2O_3 sample is implanted only by H ions. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) method is used to investigate hydrogen retention in two Al_2O_3 samples.

Single-crystal α-Al_2O_3 wafers with dimensions of $5\times5\times0.5$ mm^3 are (0001)-oriented, purchased at Shanghai Institute of Optics and Mechanics, Chinese Academy of Sciences. With the irradiation surface polished, Al_2O_3 samples are irradiated and implanted along the direction with an angle of 7° from the (0001) orientation to minimize the channeling effects. Here we use hydrogen instead of tritium for the reasons of convenience and their similar properties. Figure 1(a) shows two types of Al_2O_3 samples: the Au+H sample is irradiated by Au ions followed by H ions implantation, and the single H sample is only implanted by H ions. The depth profiles of H ion concentration and Au ions irradiation damage simulated by stopping and range of ions in matter (SRIM) code[16] are shown in Fig. 1(b). The projected range of H ions simulated by the SRIM code is 1020 nm. Au ion irradiation produces a peak damage of around 21 displacement per atom (dpa) at the depth of around 500 nm from the irradiation surface in Al_2O_3. The 4 MeV Au^{2+} ions with a fluence of 4.4×10^{15} cm^{-2} are produced by the facility of 2×1.7 MV tandem accelerator at Peking University. H^+ ions are produced by an accelerator at

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Beijing Normal University with the energy and fluence of 190 keV and 1.0×10^{17} cm^{-2}, respectively. The aim is to compare the hydrogen retentions over the depth range of Au ion irradiation damage in the Au+H sample and the single H sample to investigate the influence of irradiation damage on the TPRP of Al_2O_3.

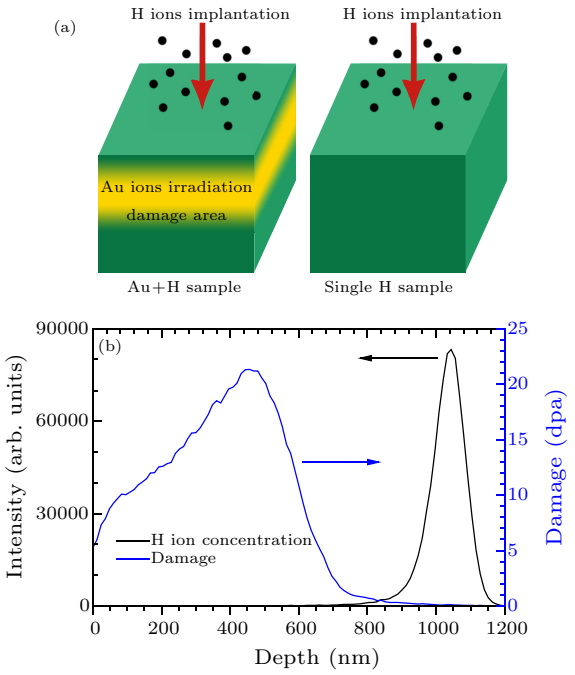

Fig. 1. (a) Irradiation and implantation into Al_2O_3. The Au+H sample is irradiated by Au ions followed by H ion implantation (left), while the single H sample is only implanted by H ions (right). (b) Depth profiles of H ion concentration and Au ion irradiation damage simulated by the SRIM code, in units of dpa (displacement per atom).

The TOF-SIMS experiments are carried out on a TOF. SIMS 5-100 spectrometry at Tsinghua University with an acceptable systematic error of 5%, and both the Au+H sample and the single H sample are under the same experimental conditions. The TOF-SIMS method is sensitive to hydrogen detection, through which the relative single hydrogen (^{1}H) depth profile can be obtained, while the quantitative information of hydrogens in Al_2O_3 is unavailable. The experiments are carried out under 1.9×10^{-7} Pa vacuum to avoid high hydrogen background. Background hydrogens covered on the Al_2O_3 sample surface are acceptable with a concentration in the order of 10^{17} atom/cm^3, while the concentrations of implanted hydrogens range from 10^{18} atom/cm^3 to 10^{21} atom/cm^3 over the depth range of H implantation, which are calculated by the SRIM code. What is more, primarily ionic groups such as OH^- and OH_2^- rather than single hydrogen are detected to obtain the hydrogen retention in Al_2O_3. In TOF-SIMS, IMS is an important tool to analyze the sputtered ions and ionic groups, such as H^- and OH^-. However, in IMS we only obtain the atomic weight, 17 for example, and it corresponds to OH^- or $^{17}O^{2-}$, which seems hard to decide the exact ion. Luckily, the natural atom ratio of ^{16}O, ^{17}O and ^{18}O is known, thus the amounts of ^{17}O and ^{18}O can be calculated when the amount of ^{16}O is given, which means that we can tell OH^- from $^{17}O^{2-}$ when an atomic weight of 17 is given. Using the same method, we can extract data related to hydrogen when other atomic weights are given. When H ions are implanted into the Al_2O_3 sample, some of them may interact with Al_2O_3 to form ionic groups such as OH^- or OH_2^-.[15] Irradiation defects act as hydrogen traps to attract hydrogen around them,[17] therefore probably larger quantities of hydrogen are retained in Au ion irradiated Al_2O_3. When the amounts of single hydrogen and hydrogen from ionic groups at a certain depth are added, we obtain the hydrogen retention. Over the depth range of Au ion irradiation, the hydrogen retentions in the Au+H sample and the single H sample are compared to investigate the influence of irradiation damage on the TPRP of Al_2O_3. The transmission electron microscopy (TEM) method is used for investigating the irradiation damage produced by Au ions in Al_2O_3, with an FEI Tecnai F20 electron microscope operating at 200 kV at the electron microscopy laboratory of Peking University. Cross-sectional specimens were mechanically thinned and polished on both sides to thicknesses of 20–30 μm, followed by 4.5 keV Ar^+ ion milling to obtain thinner region for the TEM experiment. Additionally, the Rutherford backscattering spectrometry/channeling (RBS/C) method is used to obtain Au-ion-induced damage in Al_2O_3 with a collimated 2 MeV He^+ beam. The energy resolution is 15 keV.

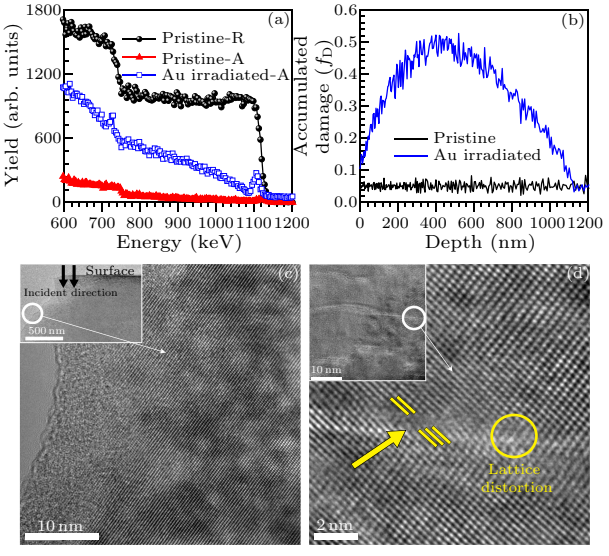

Fig. 2. Irradiation damage in Al_2O_3. (a) RBS spectra recorded in random and (0001)-axial directions on Al_2O_3. (b) Damage depth profiles in Al_2O_3 extracted from the analysis of RBS spectra of (a). Cross-sectional TEM micrographs of (c) the pristine Al_2O_3 sample and (d) the Au ion irradiated Al_2O_3 sample at the depth of around 500 nm. Here f_D refers to the fraction of displaced atoms indicating the degree of accumulated damage.

Figure 2(a) displays the RBS/C spectra of pristine

and Au ion irradiated samples recorded with 2 MeV He ions. The random and aligned RBS/C spectra of the pristine sample is for comparison. Two plateaus (below energies 1150 and 750 keV) correspond to the backscattering of He ions from Al and O atoms of the target, respectively. The increase of the backscattering yield observed in the aligned spectra around energies 1100 and 730 keV attests to the creation of displacement damage by Au ion irradiation in Al and O sublattices. Assuming that the RBS/C yield is proportional to the number of displaced atoms, the depth distributions of the accumulated damage (f_D) in both pristine and Au ion irradiated Al_2O_3 extracted from a computer program DICADA[18] (dechanneling in crystals and defect analysis) are shown in Fig. 2(b). The accumulated damage is below 1, indicating that the irradiated region is not amorphous.[19] In the pristine sample, the accumulated damage is steadily 0.05 as an original damage level. Therefore, irradiation damage produced by Au ions extends from the surface to around 1100 nm. The measured depth profile of Au ion irradiation damage obtained from RBS/C experiments shown in Fig. 2(b) is deeper than the one simulated by the SRIM code in Fig. 1(b), which is proved by the results of Shi *et al.*[20] and Kuri *et al.*[21,22] Therefore the measured damage profile obtained from the RBS/C experiments will be used to investigate the effects of irradiation damage on the TPRP of Al_2O_3. It is noteworthy that the calculated peak damage created by H ion implantation is 0.5 dpa, which is negligible compared with the Au ion irradiation damage. Figures 2(c) and 2(d) illustrate cross-sectional TEM micrographs of the pristine and Au ion irradiated Al_2O_3 samples respectively at the depth of 500 nm. Figure 2(c) shows a perfect single crystal state of pristine Al_2O_3, while the amorphous state appearing in the marginal area is induced by the ion milling irradiation damage. As shown in Fig. 2(d), Au ion irradiation produces local lattice distortion. The lattice distortion creates a local strain field, which may interact with that of implanted hydrogen, attracting hydrogen around the distortion area. Dislocation produced by Au ion irradiation is observed near the lattice distortion. The strain field of dislocation also has a potential to trap hydrogen, and thus has an effect on the hydrogen retention in Al_2O_3.

The single hydrogen depth profile obtained from the TOF-SIMS experiment is shown in Fig. 3. Here the single hydrogen depth profile does not involve the hydrogen combined to Al_2O_3. Figures 3(a) and 3(b) show the Gaussian distributions of single hydrogen in the Au+H sample and the single H sample, respectively, with the projected ranges of around 980 nm. The projected range simulated by the SRIM code is 1020 nm, proving that the experimental error is in the acceptable scope. Hydrogen penetrates through the depth range of Au ion irradiation, probably interacting with irradiation defects, which will be discussed.

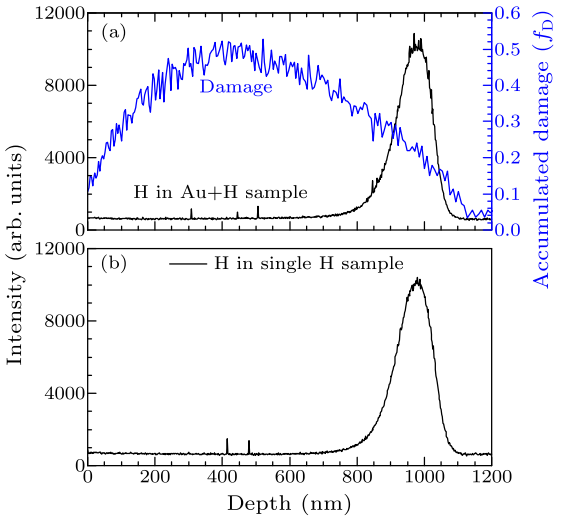

Fig. 3. The single hydrogen depth profile in Al_2O_3 obtained from the TOF-SIMS experiment. (a) Single hydrogen depth profile and Au ion irradiation damage depth profile in the Au+H sample. (b) Single hydrogen depth profile in the single H sample.

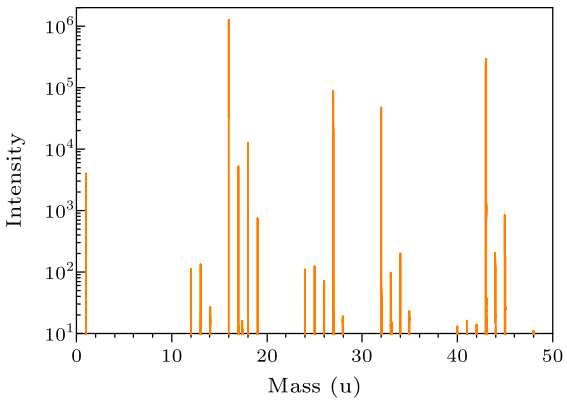

Fig. 4. Ions mass spectra of the Au+H sample at a depth of around 500 nm.

Al_2O_3 has a great hydrogen isotope PRF factor due to its low hydrogen permeability limiting the diffusion of hydrogen, on the other hand defects such as dislocations and vacancies will interact with hydrogen impeding its transport in Al_2O_3, which is proved by the work of Zhang *et al.*[12] Interaction between hydrogen and defects will impede the migration of hydrogen, therefore strengthening the TPRP of Al_2O_3. Defects interact with hydrogen in two ways: physical traps and chemical traps. Some defects such as dislocations and vacancies have strain field around them. The strain field will interact with that of hydrogen, which will trap hydrogen around these defects called physical traps. Chemical traps refer to atoms or interstitials that have dangling bonds. SiC, another TPB, also have low hydrogen diffusivity due to its chemical traps.[23] The C- and Si-dangling bonds interact with hydrogen to form chemical bonds, impeding the diffusion of hydrogen. For Al_2O_3, chemical traps such as O interstitials can easily combine to hydrogen to form hydroxyls by strong chemical bonds,[15] limiting the

migration of hydrogen and strengthening the TPRP of Al_2O_3. Figure 2(d) shows that ion irradiation produces substantial irradiation defects such as dislocations and interstitials, with corresponding vacancies produced while they could not be seen through TEM. That is, ion irradiation produces plenty of physical and chemical traps, probably improving the TPRP of Al_2O_3. Figure 4 shows an IMS of the Au+H sample at a depth of around 500 nm. When eliminating the effects of ^{17}O and ^{18}O mentioned above, it could be seen that implanted hydrogen either remains the form of single hydrogen or mainly combines to oxygen in forms of OH^- or OH_2^- corresponding to the atomic weights of 17 and 18, respectively, which is in accord with the results of Moroño *et al.*[15] Other forms seem to be $Al_xO_yH_z$, where x, y and z are integers. Similar results are seen in the single H sample. However, more ionic groups such as OH^- form in the Au+H sample, probably affected by the chemical traps produced by Au ion irradiation, proving that ion irradiation enhances the retention of hydrogen in Al_2O_3. Total amounts of hydrogen over the depth range of Au ion irradiation in the Au+H sample and the single H sample will be compared to prove the hydrogen retention enhancement caused by the ion irradiation.

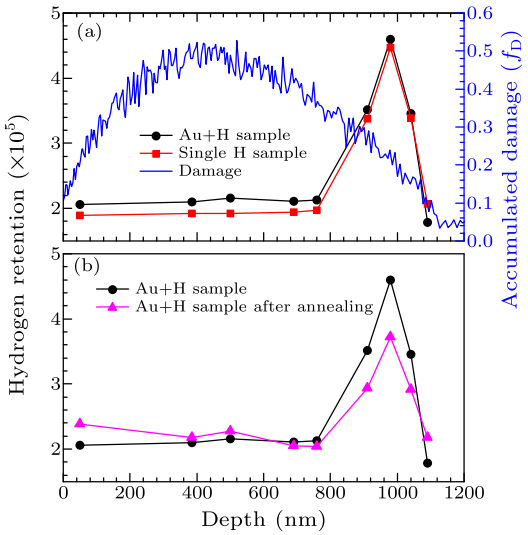

Fig. 5. (a) Hydrogen retentions as a function of depth in the Au+H sample and the single H sample. (b) Hydrogen retentions as a function of depth before and after annealing at 773 K for 1 h in the Au+H sample.

Table 1. H/Al ratios in Au+H and single H samples.

Depth (nm)	50	385	500	690	760	910	980	1040	1090
H/Al-Au+H	1.88%	1.93%	2.10%	1.99%	2.06%	34.33%	44.74%	33.11%	1.76%
H/Al-single H	1.78%	1.80%	1.87%	1.88%	1.90%	32.12%	43.12%	32.27%	2.08%

In Fig. 4, when all hydrogen containing those combined to Al_2O_3 are added, we obtain the hydrogen retention at the depth of around 500 nm in the Au+H sample. Using the same method, we calculate the hydrogen retentions in the Au+H sample and the single H sample at the depths of 50 nm, 385 nm, 500 nm, 690 nm, 760 nm, 910 nm, 980 nm, 1040 nm and 1090 nm, among which the hydrogen range (980 nm) and full width at half maximum (910 nm and 1040 nm) refer to the single hydrogen depth profile shown in Fig. 3. Figure 5(a) shows the hydrogen retentions as a function of depth in the Au+H sample and the single H sample. The hydrogen retention is actually the experimental intensity, thus it is not representative of absolute amounts of hydrogen. As we only compare the hydrogen retentions in two samples, the relative hydrogen retention is enough for our research. Over the depth range of Au ion irradiation ranging from the surface to around 1040 nm, the hydrogen retention in the Au+H sample is greater than that in the single H sample, proving that irradiation damage improves the TPRP of Al_2O_3. The hydrogen retention is 12.5% greater at 500 nm while 2% greater at 1040 nm in the Au+H sample. The percentage increase of hydrogen retention is proportional to the Au ion irradiation damage, indicating the strong interaction between irradiation defects and hydrogen. A high density of irradiation defects may strengthen the hydrogen trap effects. Irradiation damage at 1090 nm tends to 0.05 (original damage level), and the hydrogen retention is smaller in the Au+H sample as most implanted H ions keep within 1040 nm. To calibrate the amount of ^1H by Al, the H/Al ratios obtained from TOF-SIMS experiments in both Au+H and single H samples are listed in Table 1 to reflect the validity of data in Fig. 5(a). H/Al ratios at each depth in the two samples exhibit the same size relationship as hydrogen retentions in Fig. 5(a), reflecting the validity of size relationship of hydrogen retention in Fig. 5(a). The result here is significant in the research of TPB. Al_2O_3 suffers from severe irradiation while it is probably beneficial to its TPRP according to our results. Usually irradiation damage leads to a weakening of structural materials in the fission reactor. The result of Al_2O_3 is unusual and interesting. A similar result is seen in the electron irradiated Al_2O_3 sample.[15] They show that the ionizing irradiation strengthens the chemical reaction process between hydrogen isotopes and Al_2O_3, enhancing the hydrogen retention in Al_2O_3. However, they have not found out the nature of the interaction between hydrogen and Al_2O_3. For ion irradiation, we attribute the interaction to physical and chemical traps. Irradiation defects such as interstitials, vacancies and dislocations act as physical and chemical traps to attract hydrogen around them, enhancing the hydrogen retention in Al_2O_3.

Recently, Kobayashi *et al.* have investigated the effects of irradiation induced defects on the tritium

retention in Li_2TiO_3, i.e., a tritium breeding material in the fusion reactor.[24,25] Neutron irradiation produces two kinds of tritium traps, that is, oxygen vacancy (F^+-center) and oxygen atom with dangling bonds (O^--center), among which O^--center plays a key role in affecting the tritium retention by trapping tritium to form a hydroxyl group. An enhancement of tritium retention in neutron irradiated Li_2TiO_3 has been seen, compared with the case in pristine Li_2TiO_3. As the neutron fluence increases, the tritium retention is enhanced due to the increasing irradiation damage density. After annealing at 650 K, tritium retention in Li_2TiO_3 decreases dramatically as irradiation defects annihilate and trapped tritium releases from defects.

Inspiringly, we assume that the variation of hydrogen retention has a connection with the evolution of hydrogen traps under annealing. Thus we investigate the change of hydrogen retention in the Au+H sample after annealing at 773 K for 1 h to further study the evolution of hydrogen traps. Figure 5(b) depicts the hydrogen retentions as a function of depth before and after annealing in the Au+H sample. It is assumed that the variation of hydrogen retention under annealing is controlled by a competition mechanism: the diffusion process against the trap release process. The diffusion process refers to the normal hydrogen diffusion under annealing without the trapping effects of irradiation defects, while the trap release process refers to the hydrogen release from physical and chemical traps. Hydrogen aggregated at the depth of 980 nm diffuses inward and outward, leading to the decrease of hydrogen retention here. Hydrogen retention increases slightly at 1090 nm while decreases slightly at 690 nm and 760 nm. Without the trapping effects of irradiation defects, the diffusion process will enhance the hydrogen retention at 690 nm and 760 nm due to the increasing hydrogen diffused from the depth of 980 nm. The opposite result is a consequence of the trap release process. As shown in Fig. 5(a), irradiation damage at 690 nm and 760 nm is less severe, and irradiation defects here will annihilate more easily under annealing condition, thus the trapped hydrogen will release from physical and chemical traps, leading to the decrease of hydrogen retention. It is inferred that the trap release process of the competition mechanism dominates, making the hydrogen retentions at 690 nm and 760 nm smaller after annealing. The irradiation damage is much more severe with high defect density around 500 nm, usually meaning that defects will interact with each other to stabilize. What is more, hydrogen trapping efficiency is increased at high defect density area.[24] Therefore, defects annihilation process and trap release process are weaker under annealing condition, hardly affecting the hydrogen retention. The diffusion process dominates and the hydrogen retention increases slightly around 500 nm. At 50 nm, hydrogen retention increases sharply after annealing. It is speculated that defects migrate to aggregate with other defects to form large and stable defects such as voids and pores under annealing at near surface area, trapping more diffused hydrogen. On the other hand, contamination caused by annealing may contribute to the hydrogen retention increase at 50 nm. In short, hydrogen traps produced by Au ion irradiation have a positive impact on the hydrogen retention in Al_2O_3, enhancing the TPRP of Al_2O_3.

In summary, over the depth range of Au ion irradiation, the hydrogen retention in the Au+H sample is greater than that in the single H sample, showing that ion irradiation damage improves the TPRP of Al_2O_3 under given conditions. The enhancement of hydrogen retention in the Au+H sample is attributed to the interaction between hydrogen and physical and chemical traps. Irradiation defects such as interstitials, vacancies and dislocations produced by Au ion irradiation act as physical and chemical traps to attract hydrogen around them, enhancing the hydrogen retention in the Au+H sample. Comparing the hydrogen retentions before and after annealing at 773 K for 1 h in the Au+H sample, it is found that hydrogen traps produced by Au ion irradiation do have a positive impact on the hydrogen retention in Al_2O_3.

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