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XPS analysis on chemical states of Li_4SiO_4 irradiated by 3 keV D_2^+

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ABSTRACT

Li_4SiO_4 will be applied as tritium breeding materials in future fusion reactor. The release behavior of tritium from neutron-irradiated Li_4SiO_4 should be sensitive to the chemical states of lithium, oxygen and silicon on the surface of Li_4SiO_4 with irradiated defects. The present study is focused on the influence of hydrogen isotopes and irradiation defects on surface chemical state of Li_4SiO_4. The X-ray Photoelectron Spectroscopy (XPS) was compared between non-irradiated Li_4SiO_4 and D_2^+-irradiated one. It was observed by that the binding energy (BE) of electron for Li-1s, O-1s and Si-2p of non-irradiated Li_4SiO_4 were 60.9 eV, 536.1 eV and 107.1 eV respectively. However new XPS peak for Li-1s at 57.2 eV, three XPS peaks for O-1s (at 536.1 eV, 533.2 eV and 531.3 eV, respectively) and three XPS peaks for Si-2p (at 107.1 eV, 104.2 eV and 99.7 eV, respectively) were observed in D_2^+-irradiated Li_4SiO_4. It is considered that the XPS peaks of 531.3 eV and 104.2 eV should be corresponding to O-1s and Si-2p in –Si–O–D while the XPS peak of 533.2 eV should be corresponding to O-1s in D–O–D. The formation of –Si–O–D and D–O–D is considered to be due to typical irradiated defects (lithium vacancy, silicon vacancy and implanted deuterium) induced by D_2^+-irradiation.

1. Introduction

In ITER test blanket module design, the elucidation of tritium recovery from solid tritium breeding material is one of critical issues for TBM design. The study of hydrogen isotopes behavior in solid breeding materials is one of the most important subjects in the design of test blanket module. There are a variety of ternary lithium oxides such as Li_4SiO_4 and Li_2TiO_3 that could be employed as a candidate solid breeding materials for D–T fusion reactor. Okuno et al. [1–4], Oya et al. [5–7] and Tanaka et al. [8–13] have carried out some studies on behaviors of hydrogen isotopes in these ternary lithium oxides. Li_4SiO_4 will be applied as tritium breeding materials in EU helium cooled pebble blanket (HCPB) and CN helium cooled solid blanket (HCSB). Tritium should be released as HTO or HT from surface of Li_4SiO_4 after neutron irradiation. And the ratio of tritium released as HTO to HT is one of key parameters for establishment of tritium extraction system in fusion reactor. The release chemical form of tritium should be determined by surface chemical environment of Li_4SiO_4 affected by various radiation defects.

The typical irradiation defects induced by neutron irradiation in Li_4SiO_4 are considered to consist of Li vacancy, Si vacancy and F-centers (oxygen vacancy with one or two electrons). The formation of Li vacancies is considered to be mainly due to the breeding reaction between neutron and lithium. And the displacements induced by neutrons irradiation or/and products of breeding reaction such as helium and tritium ions with high energy of about 2 MeV can provide Si vacancies, F-centers and some Li vacancies. Tritium produced by breeding reactions in Li_4SiO_4 can be located at Li vacancy to turn into the substitutional T^+ for Li^+ (sub. T_{Li}^+) and at Si vacancy to the substitutional T^+ for Si (sub. T_{Si}^+). Tritium can also be located at an interstitial site to turn into the interstitial T^+ (int. T^+). Therefore there are three possible states of T^+ in Li_4SiO_4 after neutron irradiation, namely sub. T_{Li}^+, sub. T_{Si}^+ and int. T^+. All of T^+ (whether sub. T^+ or int. T^+) will be attracted by neighboring oxygen ions to form the $-OT^-$ of sub. T^+ or int. T^+ [1–4,12,13].

However the experiments of neutron irradiation or tritium ions irradiation are difficult to be performed. Hence the D_2^+-irradiation has been applied as a technique of hydrogen isotopes implantation. It is considered that the displacements or sputtering by D_2^+-irradiation can provide Li vacancies, Si vacancies, and F-centers. D_2^+-irradiation can also induce the deuterium as sub. D_{Li}^+, sub. D_{Si}^+ and int. D^+ which is similar to the case of tritium in neutron irradiation. All of D^+ (whether sub. D^+ or int. D^+) will be attracted by neighboring oxygen ions to form the $-OD^-$ of sub. D^+ or int. D^+ [8–13].

Some surface analysis methods combined with deuterium implantation technical have contributed to the study on release behavior of hydrogen isotopes from various ternary lithium oxides affected by irradiation defects [1–13]. It has been observed that deuterium implanted into Li_4SiO_4 can be desorbed as hydrogen molecular forms (D_2/HD) and water forms (D_2O/HDO), which is corresponding to that tritium produced in neutron-irradiated Li_4SiO_4 can be released as HT and HTO. From the viewpoint of tritium extraction system, desorption of tritium as hydrogen molecular forms means higher safety and efficiency than that as water forms.

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Desorption of hydrogen isotopes as water forms and/or hydrogen molecular forms might be due to the existence states of hydrogen isotopes on the surface of irradiated Li_4SiO_4. However it is difficult to observe the existence states of hydrogen isotopes directly. To analyze the existence states of hydrogen isotopes indirectly, the present study was focused on the chemical states of other elements such as Li, O and Si on the surface of Li_4SiO_4 affected by hydrogen isotopes and irradiation defects. Deuterium ion implantation (3 keV D_2^+-irradiation) was used to induce hydrogen isotopes (deuterium instead of tritium) and other irradiation defects into the surface of Li_4SiO_4. The chemical states of lithium (Li-1s), oxygen (O-1s) and silicon (Si-2p) were checked by X-ray Photoelectron Spectroscopy (XPS) before and after D_2^+-irradiation respectively.

2. Experimental

2.1. Material

The Li_4SiO_4 powder prepared by solid reaction method in Southwestern Institute of Physics (SWIP) (total content of impurity elements <0.1%, monoclinic phase purity of Li_4SiO_4 > 98%) was sintered to a plate with the diameter of about 10 mm and the thickness of about 1 mm in Shizuoka University.

2.2. Experimental methods

The apparatus in Shizuoka University consists of two vacuum chambers connected to each other via a gate valve and one sample-loading chamber. One vacuum chamber (signed as T-chamber) is equipped with heating system, Quadrupole Mass Spectrometer (QMS) and ion guns, and the other (signed as X-chamber) is with X-ray Photoelectron Spectroscopy (XPS) ESCA 5800 manufactured by ULVAC PHI Inc. Both T-chamber and X-chamber are evacuated to less than 10^{-8} Pa using ion pumps. The Kα of Al was used for X-ray source.

Firstly the sintered Li_4SiO_4 plate was sent to T-chamber by the one sample-loading chamber. Before D_2^+-irradiation the preheating treatment for Li_4SiO_4 plate was performed at 1000 K for 3 h in T-chamber to remove volatile compounds impurities in the sample. When the sample was cooled down to room temperature (R.T. about 300 K), it was sent to X-chamber by sample-loading chamber. The Li-1s, Si-2p and O-1s XPS spectra on the surface of original Li_4SiO_4 plate were obtained as the basis of comparison.

Secondly the sample was sent back to T-chamber and 3 keV D_2^+-irradiation with the fluence of 1.0×10^{22} D^+ m^{-2} and the flux of 2×10^{18} D^+ m^{-2} s^{-1} was conducted to the sample. The ion implantation depth of the corresponding 1.5 keV D^+ was about 50 nm according to calculation by SRIM2003 code, which is sufficient for XPS. After irradiation the sample was sent to into X-chamber and the Li-1s, Si-2p and O-1s XPS spectra on the surface of D_2^+-irradiated Li_4SiO_4 plate were checked respectively.

Thirdly the sample was sent back to T-chamber to be heated to 1000 K with the heating rate of 5 K/min and kept at 1000 K until no deuterium is released from the sample, which is called as heating recovery process. During heating recovery process thermal desorption spectroscopy (TDS) of deuterium from irradiated Li_4SiO_4 was observed by QMS. After the sample was cooling down to R.T. in vacuum, it was sent into X-chamber and the Li-1s, Si-2p and O-1s XPS spectra on the surface of Li_4SiO_4 were checked respectively again.

3. Results

The Li-1s XPS spectra of Li_4SiO_4 before D_2^+-irradiation, after D_2^+-irradiation and after heating recovery process are compared in Fig. 1. The binding energy of electron (BE) for Li-1s is mainly observed at 60.9 eV before D_2^+-irradiation. And that is shifted to 57.2 eV after 3 keV D_2^+-irradiation at R.T. and shifted back to 60.9 eV after TDS. The shifting of BE for Li-1s is considered to be due to the change of chemical state of lithium on the surface of Li_4SiO_4 by D_2^+-irradiation. For convenience the XPS peak for Li-1s at 60.9 eV is labeled as Li-α and that at 57.2 eV as Li-β.

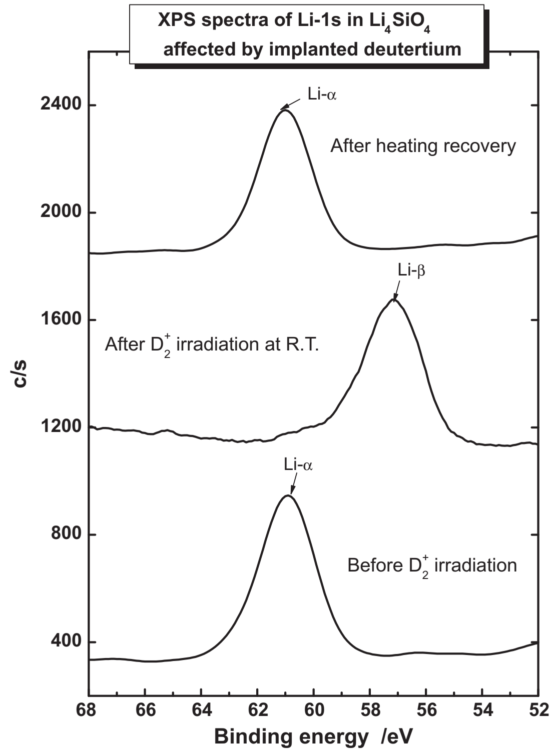

Fig. 1. XPS spectra of Li-1s in Li_4SiO_4.

The O-1s XPS spectra of Li_4SiO_4 before D_2^+-irradiation, after D_2^+-irradiation and after heating recovery process are compared in Fig. 2. The binding energy of electron (BE) for O-1s is mainly observed at 536.1 eV before D_2^+-irradiation. And multiple XPS peaks for O-1s are observed at the range of 530–540 eV after 3 keV D_2^+-irradiation at R.T. It is considered that the XPS spectra of O-1s after irradiation consist of three XPS peaks, namely, the first is at 536.1 eV, the second is at 533.2 eV, and the third is at 531.3 eV. It is also observed that the XPS spectra of O-1s almost recovered after heating recovery process. However the asymmetry of XPS peak for O-1s indicates that there might be a new small XPS peak for O-1s at about 538 eV after TDS. For convenience the XPS peak for O-1s at 536.1 eV is labeled as O-α, that at 533.2 eV as O-β and that at 531.3 eV as O-γ.

The Si-2p XPS spectra of Li_4SiO_4 before D_2^+-irradiation, after D_2^+-irradiation and after heating recovery process are compared in Fig. 3. The binding energy of electron (BE) for Si-2p is mainly observed at 107.1 eV before D_2^+-irradiation. And multiple XPS peaks for Si-2p are observed at the range of 95–110 eV after 3 keV D_2^+-irradiation at R.T. It is considered that the XPS spectra of Si-2p after irradiation consist of three XPS peaks, namely, the first is at 107.1 eV, the second is at 104.2 eV, and the third is at 99.7 eV. It is also observed that the XPS spectra of Si-2p almost recovered after heating recovery process. However the BE of main XPS peak for Si-2p (107.7 eV) after heating recovery process is about 0.6 eV higher than that before irradiation. For convenience the XPS peak for Si-2p at 107.1 eV is labeled as Si-α, that at 104.2 eV as Si-β and that at 99.7 eV as Si-γ.

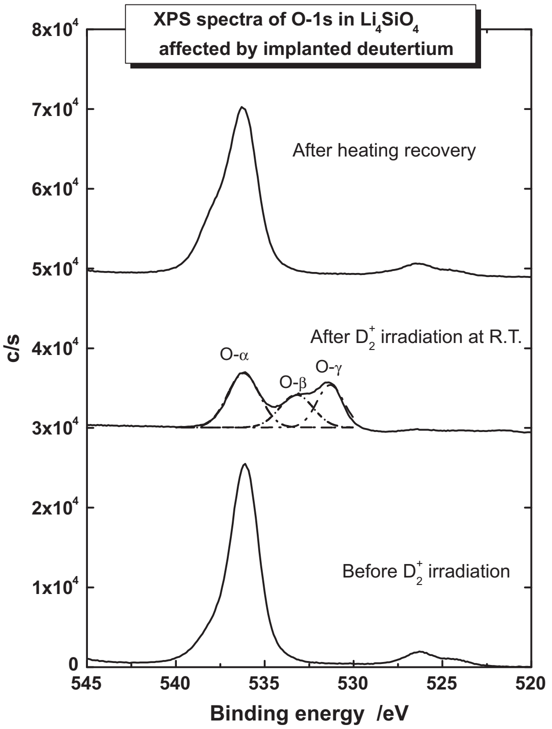

Fig. 2. XPS spectra of O-1s in Li_4SiO_4.

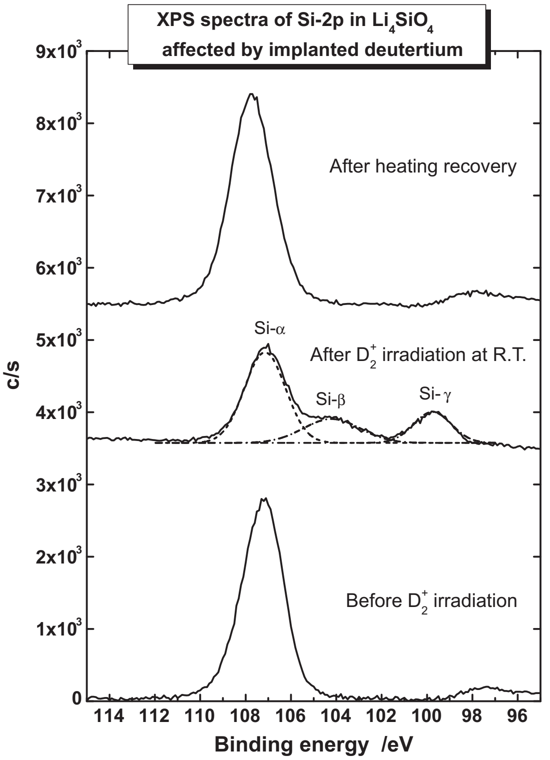

Fig. 3. XPS spectra of Si-2p in Li_4SiO_4.

The TDS of deuterium from irradiated Li_4SiO_4 during heating recovery process is shown in Fig. 4. It is observed that QMS signal of water forms (HDO and D_2O) is less than 1% of deuterium molecular forms (HD and D_2) during heating recovery process. It is indicated that most of deuterium-irradiated into Li_4SiO_4 was desorbed as hydrogen molecular forms.

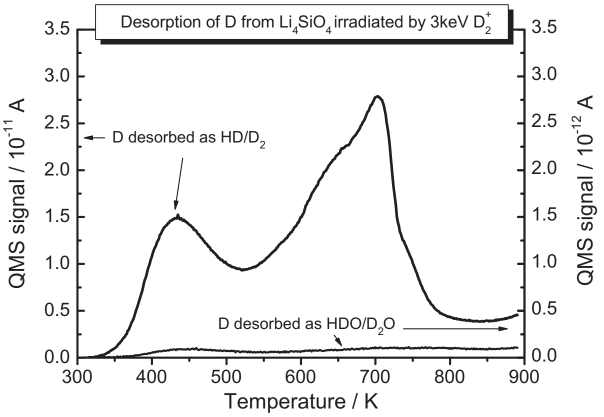

Fig. 4. TDS of deuterium from irradiated Li_4SiO_4 (left *Y* coordinate is for HD and D_2 while right *Y* coordinate is for HDO and D_2O).

4. Discussion

Since Li-α, O-α and Si-α were observed on the surface of Li_4SiO_4 before D_2^+-irradiation and recovered after the release of deuterium implanted into Li_4SiO_4, they should be assigned to the intrinsical chemical states of lithium, oxygen and silicon respectively. However it was observed that Li-α disappeared while both O-α and Si-α were partly retained after D_2^+-irradiation, which suggested that intrinsical chemical states of oxygen and silicon should be strongly associated with each other while almost not associated with that of lithium in Li_4SiO_4. Some molecular dynamics simulation on $LiAlO_2$, other ternary lithium oxides, showed that the Al–O sub-network constitutes the skeleton of the whole structure of $LiAlO_2$ while lithium cations can move within the framework with low activation energy [14]. Analogically it is considered that O-α and Si-α should indicate the bond between Si and O in SiO_4^{4-}, the which constitutes the skeleton of the whole structure of Li_4SiO_4 while Li-α should indicate the Li^+ which is binding to oxygen in SiO_4^{4-} so weak that its XPS is independent on that of Si and O in SiO_4^{4-}. Since Li-β, O-β and O-γ, Si-β and Si-γ appeared on the surface of D_2^+-irradiated Li_4SiO_4 and disappeared after the release of deuterium implanted into Li_4SiO_4, they should be assigned to the chemical states of lithium, oxygen and silicon influenced by implanted deuterium respectively.

4.1. Possible decomposition of Li_4SiO_4

One possibility is that appearance of Li-β, O-β and O-γ, Si-β and Si-γ might be due to decomposition of Li_4SiO_4 to Li_2O and Li_2SiO_3 (even $2Li_2O$ and SiO_2) by D_2^+-irradiation. The XPS peaks for Li-1s at 53.3 eV and O-1s at 528.3 eV in Li_2O have been reported [15], which are much lower than any of Li-β, O-β and O-γ. Otherwise the ratios of both Li-β to O-β and Li-β to O-γ are calculated to more than 4:1, which is also much higher than atomic ratio of Li to O (2:1) in Li_2O. Therefore any of O-β and O-γ is considered to be not corresponding to O-1s in Li_2O while Li-β to Li-1s in Li_2O.

It should be noticed that the XPS peak for O-1s at 532.9 eV and that for Si-2p at 104 eV has been reported in SiO_2 gel [18], which are much closer to O-β at 533.2 eV and Si-β at 104.2 eV. It seems more consistent on BE that O-β and Si-β might be due to the formation of SiO_2 gel on the surface of D_2^+-irradiated Li_4SiO_4. However this assignment can not be supported by the following facts. The ratio of O-β to Si-β is calculated to be about 4.3:1, which is much higher than atomic ratio of O to Si (2:1) in SiO_2. Otherwise the disappearing of O-β and Si-β after TDS up to 1000 K is also in contradiction with high thermal stability of SiO_2. Therefore it is considered that O-β and Si-β are not corresponding to O-1s and Si-2p in SiO_2.

Based on above discussion, it is considered that decomposition of a small quantity of Li_4SiO_4 was possible however it should not be the main reason for appearance of Li-β, O-β and O-γ.

4.2. Possible formation of –Si–O–D and D–O–D

The other possibility is that appearance of Li-β, O-β and O-γ, Si-β and Si-γ might be due to some irradiation defects induced by D_2^+-irradiation into Li_4SiO_4. Typical irradiation defects that interact with deuterium implanted into Li_4SiO_4 would be Li^+ vacancy, Si^{4+} vacancy, oxygen vacancy and implanted deuterium. Deuterium-irradiated into Li_4SiO_4 can be located at Li vacancy to turn into the substitutional D^+ for Li^+ (sub. D_{Li}^+) and at Si^{4+} vacancy to the substitutional D^+ for Si^{4+} (sub. D_{Si}^+). Deuterium-irradiated into Li_4SiO_4 can also be located at an interstitial site, namely the interstitial D^+ (int. D^+). All of D^+, whether sub. D^+ (sub. D_{Li}^+ and sub. D_{Si}^+) or int. D^+, will be attracted by neighboring oxygen ions to form O–D bond [12]. The O–D bond in D_2^+-irradiated ternary lithium oxides [13] has been observed, therefore some of Li-β, O-β and O-γ, Si-β and Si-γ might be corresponding to –OD of sub. D_{Li}^+, –OD of sub. D_{Si}^+ or –OD of int. D^+.

In either –OD of sub. D_{Li}^+ or –OD of int. D^+, deuterium is regarded to be trapped by oxygen of SiO_4^{4-} group to form the bridged bonds constituted of Si, O and D (which is labeled as –Si–O–D). The XPS peak for O-1s at 531.9 eV and that for Si-2p at 103 eV has been observed in $Si(OH)_4$ [16], which are close to O-γ at 531.3 eV and Si-β at 104.2 eV. Otherwise the XPS peak for Si-2p at 102.5 eV in SiOH has been also reported [17], which is lower than that in $Si(OH)_4$. As we all know, higher positive oxidation state and higher BE. Since Si in $Si(OH)_4$ is considered to be of higher positive oxidation state than that in SiOH, it is reasonable that the BE for Si-2p in $Si(OH)_4$ is higher than that in SiOH. It suggested that the BE of XPS peak for Si-2p in –Si–OH might be increased with the increase of the ratio of O to Si. The ratio of O-γ:Si-β on the surface of D_2^+-irradiated Li_4SiO_4 has been calculated to be about 4.5:1 (the difference between the sensitivity of XPS to Si and that to O is also considered in calculation), which is close to that (4:1) in $Si(OH)_4$. It is considered that Si of –Si–O–D in the present case should be of higher positive oxidation state that in $Si(OH)_4$. Therefore the difference of BE between Si-β and Si-2p in $Si(OH)_4$ should be accepted if O-γ and Si-β are assigned to be –Si–O–D.

In –OD of sub. D_{Si}^+, deuterium can be trapped by oxygen to form the bridged bonds constituted of Li, O and D (which is labeled as –D–O–Li). The XPS peak for O-1s at the range of 531.2–531.6 eV has been observed [15] in LiOH, which seems to be consistent with O-γ at 531.3 eV. If O-γ was assigned to be O-1s in LiOD, Li-β had to be assigned to be Li-1s in LiOD. However the ratio of Li-β to O-γ is calculated to about 4:1, which is much higher than atomic ratio of Li to O (1:1) in LiOD. Therefore it is considered that O-γ and Li-β are not corresponding to O-1s and Li-1s in LiOD.

The XPS peaks for O-1s at the range of 533.1–533.2 eV has been observed in H_2O on the surface of some materials [19,20], which are consistent with O-β at 533.2 eV. It suggested that O-β might indicate the formation of D–O–D on the surface of deuterium-irradiated Li_4SiO_4. Since D_2^+-irradiation can bring so many sub. D_{Si}^+, sub. D_{Li}^+ and int. D^+, it is possible that the bridged bond as D–O–D can be formed when either sub. D_{Li}^+ or int. D^+ is neighboring to sub. D_{Si}^+. Otherwise O-β is considered to be independent on silicon and lithium, therefore O-β should be due to D–O–D on the surface of D_2^+-irradiated Li_4SiO_4.

Based on above discussion, it is considered that Si-β and O-γ are corresponding to Si-2p and O-1s in –Si–O–D respectively while O-β is corresponding to O-1s in D–O–D. The formation of –Si–O–D and D–O–D should be due to that deuterium located at lithium and silicon vacancy induced by irradiation or interstitial site was attracted by neighboring oxygen to form the bond of O–D.

4.3. Possibility on Si-γ and Li-β

Deuterium-irradiated into Li_4SiO_4 can be located at O vacancy to form Si–D or Li–D. Since the XPS peak for Si-2p at 107.1 eV in SiH_4 have been reported [18] which is far away from Si-γ at 99.7 eV, it is considered that Si-γ is not due to formation of the chemical bond between Si and deuterium. However the XPS peaks for Si-2p at the range of 98.5–100 eV in pure Si and metal silicides have been reported [18], which are corresponding to Si-γ at 99.7 eV. Therefore there are two possibilities for assignment of Si-γ, namely, one is the lithium silicides, and the other is reduced silicon atom. For the former possibility if Si-γ was assigned to be Si-2p in lithium silicides, Li-β had to be assigned to be Li-1s in lithium silicides. Silicon has much weaker electronegativity than oxygen in SiO_4^{4-}, and Li-1s in lithium silicides should be of lower BE than that in Li_4SiO_4, therefore the difference of binding energy between Li-α and Li-β can be explained well in this. However the ratio of Li-β to Si-γ is calculated to about 21:1, which is too high for the atomic ratio of Li to Si in lithium silicides. Therefore it is considered that Si-γ might be corresponding to Si-2p in reduced silicon atom with higher possibility. The formation of reduced silicon atom should be due to the atomic displacement by D_2^+-irradiation. Some silicon ions might leave their original sites after the collision with energetic deuterium particles, and finally be located at interstitial sites. Silicon ion at interstitial site might be reduced to silicon atom due to its surrounding chemical environment, which might result in that the XPS peak for pure Si was observed in the present case.

Since O-β, O-γ and Si-β have been definitely assigned as some chemical states irrelative to lithium, there are three possibilities remaining for assignment of Li-β, namely, the first is corresponding to Si-γ (such as lithium silicides), the second is pure reduced lithium atom, and the third is correlative to deuterium (such as LiD). As discussed in the assignments of Si-γ, the first possibility on lithium silicides is very low. Therefore it is considered that Li-β should be assigned as one of reduced lithium atom and lithium hydride.

The formation of lithium metal colloids has been observed in electron-irradiated Li_2O [21]. The XPS peak for Li-1s state in lithium metal colloids, which exists as Li^0, is reported in the lower energy region than that for Li^+ [10,22], which is consistent with the experimental results that the peak of Li-β is lower than that of Li-α (Li^+ in original Li_4SiO_4). It should be noticed the reported XPS peak for Li-1s at Li^0 is about 54.6 eV which is also lower that for Li-β. However this inconsistency might be explained by the influence of Li_4SiO_4 on Li-1s at Li^0. It has also reported that the XPS peak for Li-1s at Li^0 in lithium graphite is 57.3 eV which is higher than that in pure lithium [23]. Therefore Li-β might be due to the reduced lithium atom (Li^0) on the surface of D_2^+-irradiated Li_4SiO_4 with high possibility. However the possibility of Li-β assigned as Li-1s in LiD has not been discussed at present because of absence on the XPS data for LiD. Discussion on Li-β only by XPS results is difficult and therefore more other experimental and theoretical support is needed for the final assignment of Li-β. Although the assignment for Li-β has not been completed, it is affirmative that lithium on the surface of Li_4SiO_4 should be reduced by implanted deuterium, which indicated by Li-β with lower BE than Li-α.

4.4. Correlated to TDS

In the previous study it has been observed that deuterium implanted into ternary lithium oxides can be desorbed as hydrogen molecular forms (D_2/HD) and water forms (D_2O/HDO) [9–13], which is corresponding to that tritium produced in ternary lithium oxides can be released as HT and HTO. It was considered that desorption of deuterium as water forms should be due to –OD^- on the surface of ternary lithium oxides. The existence of –OD^- in deuterium-irradiated ternary lithium oxides has been supported by the FT-IR technique on observation of O–D vibration [9–13]. The assignments of Si-β, O-γ and O-β in the present study also suggest the existence of –OD^- in deuterium-irradiated Li_4SiO_4.

However it is observed that most of deuterium-irradiated into Li_4SiO_4 was desorbed as hydrogen molecular forms not water forms. It seems difficult to explain that deuterium exists as –OD^- can mainly be desorbed as D_2 or HD. The possibility that some deuterium-irradiated into ternary lithium oxides exist as non-O–D states (such as D^0 and D^-) has been considered to explain desorption of deuterium as HD or D_2 [12]. The presence of T^- in neutron-irradiated lithium oxides, which is corresponding to D^- in the case of deuterium-irradiation, was supported indirectly by desorption of tritium as HT and T_2 [1]. However T^- or D^- has not been observed directly in previous experiments. Their existence is only assumed to explain desorption of hydrogen isotopes as hydrogen molecular forms. The observation of Li-β suggests another possibility that desorption deuterium as HD or D_2 might be due to the surface reaction between Li-β (whether reduced lithium atom or lithium hydride) and deuterium in –OD^-. However the above suggestion also needs further experimental evidence to support.

5. Conclusions

In order to understand the possible influence on surface chemical environment of Li_4SiO_4 by hydrogen isotopes and irradiation defects, the chemical states of lithium (Li-1s), oxygen (O-1s) and silicon (Si-2p) in Li_4SiO_4 were checked by the X-ray Photoelectron Spectroscopy (XPS) before and after 3 keV D_2^+-irradiation respectively. It was observed by X-ray Photoelectron Spectroscopy (XPS) that the binding energy (BE) of electron for Li-1s, O-1s and Si-2p in non-irradiated Li_4SiO_4 were 60.9, 536.1 and 107.1 eV respectively. However new XPS peak for Li-1s at 57.2 eV, three XPS peaks for O-1s (at 536.1 eV, 533.2 eV and 531.3 eV, respectively) and three XPS peaks for Si-2p (at 107.1 eV, 104.2 eV and 99.7 eV, respectively) were observed in D_2^+-irradiated Li_4SiO_4. It is considered that the XPS peaks of 531.3 eV and 104.2 eV should be corresponding to O-1s and Si-2p in –Si-O-D while the XPS peak of 533.2 eV should be corresponding to O-1s in D-O-D. The formation of –Si–O–D and D–O–D is considered to be due to typical irradiated defects (lithium vacancy, silicon vacancy and implanted deuterium) induced by D_2^+-irradiation.

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