Study of helium evolution in nanocrystalline titanium films by slow positron beam analysis

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Abstract. In this paper, the evolution and depth profiles of vacancy-type defects were investigated by slow positron beam (SPB) analysis. Films of helium-contaminating titanium were deposited on Si substrates by direct current magnetron sputtering under the helium/argon (He/Ar) gas ambiance. Different helium concentrations were introduced into the sample films by altering the He/Ar inflow ratios ($Q_{He}/Q_{Ar}$). It was found that the defect-characteristic parameter $S$ from positron-electron annihilation peaks rise with the increase of the ratio of $Q_{He}/Q_{Ar}$. Homogenous He-related defect profiles and their evolution deep into around ~400nm were found by SPB measurements, together with the analysis of Rutherford backscattering (RBS) and elastic recoil detection (ERD).

1. Introduction
Helium can be produced in tritium storage materials and structural materials of fission reactors, accelerators and future controlled fusion reactors. Its insolubility and high mobility of the helium in the materials are crucial to study its formation and evolution in materials. Helium atoms can not be naturally dissolved in the materials, but are easily trapped by dislocation, vacancies and voids. With the increment of helium concentration, helium bubbles in the materials will be formed by migrating, diffusing and coalescence of helium atoms. Helium may change microstructure of the materials, and even cause serious degradation of some macroscopic mechanical properties of the materials, such as swelling and helium-induced brittleness[1-3]. Therefore, studies of the behavior of helium in materials are critically important in material applications. However, helium behavior studies in materials are quite complicated, many problems, such as the evolution of helium-related defects and mechanism of helium brittleness, are still under investigation.

There are three traditional methods to artificially introduce helium into materials: tritium ageing [4], neutron irradiation [5] and helium ion implantation [6]. In recent years, a magnetron sputtering technique [7-9] which works in a mixture of helium (He) and argon (Ar) gas ambient has been developed. This method can introduce helium into the growing metal films. It has many advantages, such as controllable helium concentration and a uniform He distribution in depth.

Many experiments have been used to study the behavior of helium in titanium film. As a sensitive method for studying vacancy-like defects, positron annihilation technique has been effectively
employed to probe microscopic characteristics of defects, such as concentration, size, charge states and chemical surroundings [10, 11] of the defects. Studies on helium behavior in metal films by SPB technique [8, 9] have been carried out in recent years. In this paper, He-Ti films with different helium concentrations were prepared by the magnetron sputtering technique. The methods of RBS and ERD analysis were used to determine the thickness and helium depth profile in the films, respectively. The SPB analysis was adopted to study the evolution of helium-related defect in the titanium films.

2. Experiment
The Ti films containing helium were deposited on the silicon (100) pieces by the magnetron sputtering coating equipment [8, 9]. A thin Pd layer (∼10nm) was deposited onto the surface of Ti film in order to avoid surface contamination and He-Ti layer oxidization. With different ratios of helium and argon influx rates (Q_{He}/Q_{Ar}), various He-content samples were deposited on the silicon (Si) pieces for further analysis experiments. The ERD and RBS measurements were carried out at the NEC 9SDH-2 tandem accelerator in Fudan University in Shanghai. The thickness of He-Ti films measured by RBS was about 470 nm for eight different He-Ti samples. The ERD results show that the helium content increases with the increment of the influx ratio of Q_{He}/Q_{Ar} and the distribution of helium is homogenous in the different depth of the Ti film. The SPB experiments were carried out in the institute of high energy physics in Beijing. The total counts of 2.0×10^5 were collected in the 511keV annihilation line at each incident energy. The value of the S-parameter was defined to be central region of the γ spectrum from 510.56 to 511.44keV divided by the total region of the γ spectrum.

3. Results
For the samples with different inflow rates of Q_{He}/Q_{Ar} (a for 0 (pure Ti); b for 1.0; c for 2.0; d for 4.0; e for 8.0; f for 12.1; g for 18.0 and h for 25.0), the S parameter as a function of positron incident energy is shown in Figure 1. The S parameter measurement results were found to be depending on the flow rate Q_{He}/Q_{Ar}. The corresponding eight solid lines in figure 1 are the fitting results of VEPFIT [12], respectively. The electron momentum information at different depth is represented by the S values. The corresponding positron mean implantation depth of different energy approximately is noted in the top of x-axis in figure 1.

When the energies of positron beam are very low (E≤1keV), positrons are mostly probing the extremely thin Pd surface protection layer. Since the protection-layers for all the eight samples are nearly the same, no obvious difference is observed among these low energy S-E curves (E≤1keV), where a higher surface S value is around 0.504 with S_{Pd}=0.494 characterizing the Pd layer. As the increasing of the positron beam energy, positrons will penetrate into the He-Ti layer and annihilate there, giving the structure-related information of the region by the corresponding specific S values. For those positron beam energies ranging from around 2keV to 10keV, all S-E curves are quite smooth and flat (except h), with S value distribution being uniform in depth. These results indicate that the defect profiles of the helium-related in these Ti films are fairly uniform. When the energies of the incident positrons are above 10keV, the S-E curves for the eight samples tend to merge. This implies that positrons are implanted dominantly into the Si substrate, giving the structural information of the Si substrate.
4. Discussions

For He-Ti layer (~2keV–~10keV) grown on substrates with different flow rates of $Q_{\text{He}}/Q_{\text{Ar}}$, an increasing, following saturation and further increment tendency of $S_{\text{He-Ti}}$ values have been observed from figure 1. When the flow rate of $Q_{\text{He}}/Q_{\text{Ar}}$ is increased from 1 to 4, a first increment tendency of $S$ values was observed compared with pure Ti film. This is because higher helium content is favoring for the penetration of more He ions into the Ti film, where the Ti vacancies will be filled by those He. After all the Ti vacancies were effectively filled by the He, further increasing of He into the Ti-film will make the excessive He aggregate. Eventually, He-Ti-vacancy complex and He bubbles will co-exist, with the bubble concentration getting higher. This induces the slow increment of $S$-values.

From Figure 1, the increasing of $S$ values became obvious, when the flow rate of $Q_{\text{He}}/Q_{\text{Ar}}$ was raised from 4 to 8 and 12.1, due to the annihilation of more positrons with the He-bubbles formed. With the increase of the flow rate of $Q_{\text{He}}/Q_{\text{Ar}}$, the size of He bubbles grows gradually and the bubble density will also increase, which gives rise to the increase of $S_{\text{He-Ti}}$ value. These results indicate that applying the flow rate of $Q_{\text{He}}/Q_{\text{Ar}}$ is more favorable for migration and aggregation of helium in growing Ti films.

Moreover, those helium atoms in the Ti lattice that localize in a specific region may be affected further by the increase of the flow rate of $Q_{\text{He}}/Q_{\text{Ar}}$ from 12.1 to 18 and 25. Larger bubbles may form through the migration and the coalescence of small bubbles. Some bubbles may grow bigger while the concentration of helium bubble will also increase upon the further helium content increment. Therefore, the magnitude of $S$ increases continuously.

Further studies will be carried out on the annealing and temperature scanning behavior of the He-Ti films. In order to understand the evolution of helium bubble and the phenomena of helium brittleness further, the other relevant techniques, such as slow positron beam lifetime measurements, the TEM and thermal desorption spectrometry, are needed to determine the size and internal pressure.
of He bubbles and their progressive evolution. In the meantime, in order to understand the physical mechanism of helium evolution further, the study of helium behavior in material by the use of Monte Carlo simulation [13, 14] is also in progress.

5. Conclusions
In this paper, helium-charged Ti films with different helium concentration were deposited by the He-Ar magnetron co-sputtering method. ERD result demonstrates the uniform distribution of helium in the bulk. The results of SPB reveal that the evolution of defects is related to helium content in He-Ti films, and it was found that the S parameter representing defect profiles of the helium-related in the Ti films increase with the influx rate $Q_{He}/Q_{Ar}$. S-E Data fitting results based on the three-layer model are in good agreement with the experimental data. Our investigations have demonstrated that SPB measurements are useful adjunct to conventional techniques in studies of the behavior of helium introduced into materials through magnetron sputter deposition in a He/Ar environment.

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