CHIN. PHYS. LETT. Vol. 28, No. 7 (2011) 077802

Bias Effects on the Growth of Helium-Containing Titanium Films *

ZHANG Li-Ran(张丽然)[1], DENG Ai-Hong(邓爱红)[1,2**], YANG Dong-Xu(杨东旭)[1], ZHOU Yu-Lu(周宇璐)[2], HOU Qing(侯氢)[2], SHI Li-Qun(施立群)[3], ZHONG Yu-Rong(钟玉荣)[4], WANG Bao-Yi(王宝义)[4]

[1] *Department of Physics, Sichuan University, Chengdu 610064*

[2] *Key Laboratory of Radiation Physics and Technology of the Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064*

[3] *Institue of Modern Physics, Fudan University, Shanghai 200433*

[4] *Laboratory of Nuclear Analysis Technique, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049*

(Received 1 December 2010)

Helium-containing titanium films were prepared on Si substrates with various biases applied by magnetron sputtering under stable He/Ar ambiance. Rutherford backscattering and elastic recoil detection analyses are used to measure the thickness of the He-Ti films and the helium depth profile, respectively. Experiments of x-ray diffraction and variable energy positron annihilation spectroscopy are carried out to investigate the microstructures of titanium films and the corresponding helium-related defects developed. The behavior of the implanted He, the microstructure of the He-Ti film and the formation of He-related defects all are affected by the substrate biases applied.

PACS: 78.70.Bj, 68.55.Ln, 07.85.Jy DOI:10.1088/0256-307X/28/7/077802

Helium can be generated in the tritium storage materials and the structural materials of the fission reactors, accelerators and future controlled fusion reactors.[1,2] The insolubility and high mobility of helium in solids make it critically important to study helium behavior and evolvement in some particular materials. Helium existing in those materials may aggregate and coalesce into bubbles, even causing so-called helium-brittleness when the concentration of helium is high enough. In fact, the microstructures of helium-containing materials can be affected dramatically by the existence of helium, which may also result in serious degradation of mechanical properties.[1−4] Therefore, research works on how helium cause problems in the related materials have become extremely important in nuclear material applications.

To investigate the impact of He on some specific materials, traditionally three methods can be used to introduce He into the host materials: tritium ageing,[5] neutron irradiation[6] and helium ion implantation.[7] In recent years, a kind of magnetron sputtering technique, which can work in the ambiance of helium (He) and argon (Ar) mixture gases, has been developed.[8−11] With this method, helium can be effectively introduced into growing metal films. Compared with the above three methods, this technique can control He concentration easily and produce uniform He distribution in depth with low irradiation-induced damage.[8−11]

Many experimental techniques can be used to characterize the behavior of the implanted He and its impact on metal films, such as Rutherford backscattering (RBS),[8−11] elastic recoil detection (ERD) analysis,[9−11] transmission electron microscopy (TEM),[9,10] thermal helium desorption spectroscopy (THDS),[8−10] x-ray diffraction (XRD)[8−10] and positron annihilation spectroscopy (PAS).[10−11] Among them, positron annihilation spectroscopy, a sensitive method for studying open-volume defects, has been effectively employed to probe the microscopic information of defects, such as their size, charge state, concentration, and chemical surrounding.[10−12] Studies on helium behavior in metal films by variable energy positron annihilation spectroscopy (VEPAS) have been carried out in recent years.[10−11]

In this work, helium-containing Ti films grown on Si substrates with various biases applied to the substrates are prepared by the magnetron sputtering technique. The RBS and ERD are separately used to measure the thickness of the Ti films and the depth distribution of the helium in Ti film. The XRD and VEPAS are used to study the effects of substrate biases on the formation of microstructure and the evolution of He-related defects in He-Ti films, respectively.

Using the magnetron sputtering coating equipment[9,10] and applying the same ratio of He and Ar influx rates (Q_{He}/Q_{Ar}), Ti films were deposited on the silicon substrates with different bias voltages applied (24, 63, 92, 121, and 151 V, namely sample A, B, C, D and E). A Ti disk (with purity 99.99% and 75 mm in diameter) was used as the cath-

*Supported by the National Natural Science Foundation of China under Grant Nos 10775102 and 10775101.

**Correspondence author. Email: ahdeng@scu.edu.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

ode target material. A discharge voltage was chosen to be 300 V and a sputtering current was selected to be 0.2 A. The working gases for dc discharge were a mixture of 99.99% purity argon and 99.99% purity helium. To avoid surface contamination, a very thin ($\sim$ 10 nm) Pd layer was deposited onto the surface of each Ti film. The thickness of He-Ti films measured by RBS was about 380 nm for the five different biased samples. The depth profiles of helium concentration in Ti films were determined by the elastic recoil detection (ERD) analysis.[9–11] The results of the ERD show that there exists a homogenous distribution of He and almost the same He concentration ($\sim$ 9 at.%) for the five corresponding Ti film samples.

The diffractometer of XRD (DX-1000) using Cu Kα x-ray source was used and it was working in a 2θ mode, scanning from 20° to 100° with a step of 0.02° and a resolution of 0.002°. Slow positron beam facilities at the Institute of High Energy Physics (Beijing) were employed for positron Doppler broadening measurements,[10–11] which were carried out in a vacuum chamber at about 10^{-6} Pa. The energy of the positron beam varied from 0.1 to 20 keV. A total count of 2.0×10^5 was collected in the 511 keV annihilation line at each incident energy. An S-parameter was defined as the ratio of the counts in the central area ($|E_\gamma - 511| \leq 0.44$ keV) to the total area of the peak, where E_γ is the energy of annihilation photon.

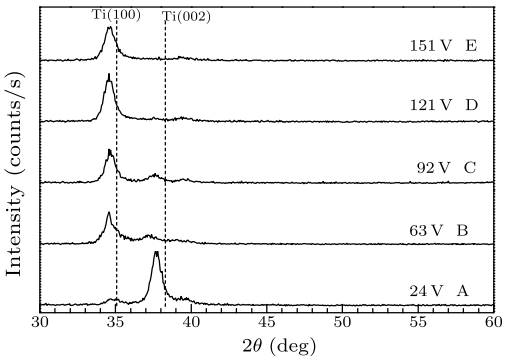

Fig. 1. XRD patterns of the Ti films with the same ratios of helium and Ar influx rates (Q_{He}/Q_{Ar}) at different substrate biases.

Figure 1 shows the XRD spectra of the He-Ti films grown under the same He/Ar ambience, but with different substrate biases applied. For pure Ti, the diffraction peaks corresponding to lattice planes of (100) and (002) should be locating at 35.1° and 38.3°, as indicated by the two vertical lines in Fig. 1. However, it is obvious that the diffraction peak from (100) plane has shifted to lower angles (from 34.9° to 34.4°) with the increase of the applied bias voltages (from 24 V of sample A to 115 V of sample E). At the same time, the corresponding intensities of the (100) diffraction peak increases with the increment of the applied bias. This observation indicates the increment of the lattice constant due to He-charging, leading to the occupation of He atoms in the interstitial positions in the Ti lattice, consequently causing lattice expansion. Similarly, the diffraction peak from the (002) lattice also shifted to lower angles, from the normal 38.3° (pure Ti) to 37.7° (sample A). In addition, it was observed that the (002) peak intensities drop dramatically from sample A (very high) to sample E (nearly disappeared), when the substrate bias increased from 24 V to 115 V. This indicates that the substrate bias could have great impact on the preferred orientation of the growth of the Ti films.

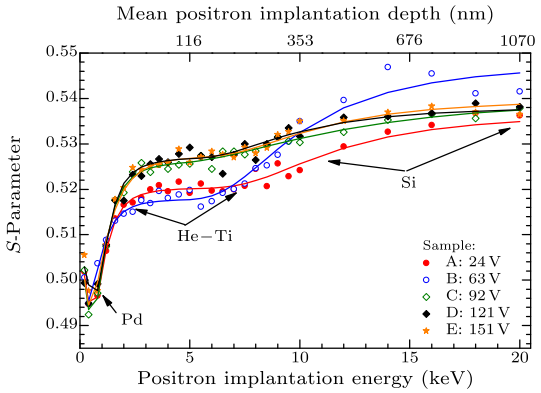

Fig. 2. The S–E curves for the Ti films with the same helium content introduced grown under various substrate biases. The solid lines are the fitting results from VEPFIT.

Figure 2 shows the S–E curves (S parameter as a function of incident positron energy) of the He-Ti films deposited on substrates with different bias voltages. The annihilation of thermalized positrons with low momentum electrons of the host material is characterized by the magnitude of S parameter.[12] In fact, the incident positron energy is related to the mean positron implantation depth. The electron momentum information at different depths is represented by the S values. The mean positron implantation depth $Z_{\rm av}$ of positrons in materials with incident energy E is taken empirically as[12] $Z_{\rm av} = 40{\rm E}^{1.6}/\rho$. The corresponding mean positron depth at different energies is noted approximately in the top horizontal axis in Fig. 2.

When the implantation energies of the positrons are very low ($E \lesssim 1$ keV), positrons probe the extreme thin protection layer of Pd and its surface. Since the protection layer for all the five samples are almost the same, no obvious difference has been observed among these S–E curves in the low energy range ($E \lesssim 1$ keV), where $S_{\rm Pd} \approx 0.495$ characterizes the Pd layer and a higher S value of $\sim$0.503 attributes to its surface. With the increasing positron beam energy, positrons will penetrate into the He-Ti layer and annihilate there, giving the structure-related information of this region by the corresponding specific

S values. For those positron beam energies ranging from around 2 keV to 8 keV (see Fig. 2), all S–E curves become smoother and flatter. These typical plateau areas, with approximately uniform distribution of S values, indicate a homogenous structure in the He-Ti film layer, which also means a uniform distribution of He-related defects. The heights of such plateaus (S values) vary from about 0.520, after a slight drop, up to 0.528 with sample substrate biases increasing from 24 V to 92 V, and keep at the same level for the following 92 V to 151 V. Thus a preliminary conclusion can be drawn that increasing the applied bias voltage during the growth of the He-Ti layer will cause an overall increment of the S values of the plateau heights, which will eventually saturate at high bias voltages. It is known that an increment of the S parameter indicates an increasing fraction of positrons annihilating with He-related defects. Such a trend may be caused by an increment of defect concentration or a change of defect type, or both. When the energies of the incident positrons are above 10 keV, further increases of S values were observed, and the S–E curves for the samples (except sample B) tend to merge and saturate. This shows that positrons were implanted dominantly into the Si substrate, giving the structural information of the Si substrate.

The above results together with those from Fudan University's research group[9–11] show that helium atoms first localize in the interstitial positions of the Ti lattice and then form helium bubbles through their diffusion and aggregation. Previous TEM studies[9,10] confirmed the existence of above 2 nm He-bubbles in those He-Ti films, when the He/Ti atomic ratio exceeds 1.2 at.%. In this study, we observed that the $S_{\mathrm{He-Ti}}$ values of the He-Ti films increase initially at lower biases, followed by the saturation of the S values at higher biases. This indicates that He aggregation by absorbing adjacent helium atoms and vacancies in the Ti lattice can be induced at low bias voltages.

When the substrate bias was increased from 24 V to 63 V, a slight drop of S values was observed. This could be explained by the higher applied bias favoring the penetration of more He ions into the Ti vacancies, which would then be filled with He. In this case, the S parameter might drop slightly due to positron annihilation with the increasing number of high-momentum electrons from helium. After all the Ti vacancies were effectively filled with He atoms upon a particular bias applied, further increase of He into the Ti-film due to the higher applied bias would make the excessive He aggregate. Eventually, a He-Ti-vacancy complex and He bubbles would co-exist, with the bubble concentration becoming higher. In Fig. 2, the increasing S values become obvious when the applied substrate bias is raised from 63 V to 92 V, due to the annihilation of more positrons at the forming He-Ti-vacancy complex or He-bubbles. With the increase of the applied bias, the size of the He-Ti-vacancy complex or He bubbles grows gradually and the concentration might also increase, both of which could cause an increase of the $S_{\mathrm{He-Ti}}$ value. This result is in agreement with the XRD observation, where the primary diffraction peaks of the Ti film shift to lower 2θ positions due to He-charging. These results show that, with a stable introduction rate of incident helium, applying a higher substrate bias would be more favorable for helium migration and aggregation in the Ti film during its early growing stage.

Naturally, it is understandable that the migration of helium ions localized in a particular region of the Ti film in a Ti lattice should be affected by a further increase of the applied biases. However, the final $S_{\mathrm{He-Ti}}$ values for higher biased samples (C, D and E) tend to saturate. No obvious changes of the S parameter were observed when the applied bias was raised from 92 V to 151 V. This indicates that, when the bias was raised to a certain value, all the He ions which might be affected by the substrate bias were fully penetrated into the Ti film and the helium-related defects in the Ti film were saturated when keeping the same He introduction rate. Some large fluctuation of $S_{\mathrm{He-Ti}}$ values for sample B has been observed when the positron beam energies are above 10 keV. This may indicate that the Si substrates of sample B have rather more open-volume defects, which may induce an abnormal S value. To clarify and understand this abnormality, re-growing the Ti film under the same condition for sample B and repeating the measurements may be necessary.

To further understand the evolution of helium bubble and the He-related brittleness of materials, more annealing positron-beam lifetime spectroscopy (PBLS), thermal helium desorption spectroscopy (THDS), and transmission electron microscopy (TEM) measurements will be employed to quantitatively obtain the information of He-related defect evolution, such as the concentration, the size and the internal pressure of He bubbles. Meanwhile, in order to understand the physical mechanism of helium evolution further, the study of helium behavior in materials by the use of Monte Carlo (MC) simulation[13,14] is also in progress.

In summary, helium-charged Ti films deposited at various substrate biases were prepared using the He-Ar magnetron co-sputtering method in this work. The results of the XRD measurements reveal that increasing the substrate bias will affect the formation of the microstructure of the grown Ti films, causing an increment of lattice constant and a change of the preferred orientation of the He-Ti films. The results of VEPAS show that the substrate bias can impact on the evolution of He-related defects and the formation

of a He-Ti-vacancy complex or He bubbles in He-Ti films. Moreover, our investigations have also demonstrated that the method of helium incorporation by magnetron sputtering in He/Ar ambience may become another experimental approach to investigate the helium behavior in materials.

References

[1] Ullmaier H 1983 *Radiat. Eff.* **78** 1
[2] Jager W, Lasser R, Schober T and Thomas G J 1983 *Radiat. Eff.* **78** 165
[3] Trinkaus H and Singh B N 2003 *J. Nucl. Mater.* **323** 229
[4] Cowgill D F 2005 *Fusion Sci. Technol.* **48** 539
[5] Weave H T and Camp W J 1975 *Phys. Rev.* B **12** 3054
[6] Rau R C and Ladd R L 1969 *J. Appl. Phys.* **40** 2899
[7] Rajainmäki H, Linderoth S S, Hansen H E, Nieminen R M and Bentzon M D 1988 *Phys. Rev.* B **38** 1087
[8] Pang H C, Luo S Z, Long X G, An Z, Liu N, Duan Y M, Wu C X, Yang B F, Wang P L and Zheng S X 2006 *Chin. Phys. Lett.* **23** 3238
[9] Shi L Q, Liu C Z, Xu S L and Zhou Z Y 2004 *Thin Solid Films* **479** 52
[10] Liu C Z, Shi L Q, Zhou Z Y, Hao X P, Wang B Y, Liu S and Wang L B 2007 *J. Phys.* D: *Appl. Phys.* **40** 2150
[11] Liu C Z, Zhou Z Y, Shi L Q, Wang B Y, Hao X P and Zhao G Q 2007 *Chin. Phys. Lett.* **24** 8
[12] Shultz P J and Lynn K G 1988 *Rev. Mod. Phys.* **60** 701
[13] Zhou Y L, Hou Q, Wang J and Deng A H 2009 *Chin. Phys. Lett.* **26** 090202
[14] Hou Q, Zhou Y L, Wang J and Deng A H 2010 *J. Appl. Phys.* **107** 084901