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**Effects of vacancy defects on the mechanical properties in
neutron irradiated Czochralski silicon**

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Abstract: We have investigated the mechanical properties of neutron irradiated Czochralski (NICZ) silicon using nanoindentation combined with micro-Raman spectroscopy. It is found that NICZ silicon shows higher hardness (~13% higher) than non-irradiated one, with a slightly lower Young's modulus. When the samples were subjected to isochronal anneals in the temperature range of 250-650 °C, the hardness of NICZ silicon gradually decreases as the temperature increases and it is finally comparable to that of non-irradiated one. The vacancies and vacancy-oxygen defects induced by neutron irradiation in NICZ silicon annihilate or transform into more complex defects during the annealing processes. It suggests that the vacancy defects play a role in the evolution of hardness, which promote phase transition from the Si-I phase to the stiffer Si-II phase in NICZ silicon during indentation. In addition, the irradiation induced vacancy defects could lead to the lower Young's modulus.

KEYWORDS: Czochralski silicon, neutron irradiation, nanoindentation, hardness,
vacancy defects

Introduction

Czochralski (CZ) silicon is a dominating semiconductor material widely used in integrated circuits, solar cells and microelectromechanical systems (MEMS), both as a structural material for MEMS devices and as a substrate material for high compatibility with semiconductor processing equipment [1]. With the increasing diameter of silicon wafers used for microelectronics industry and the increasing requirements for silicon wafer processing, the mechanical performance of CZ silicon has drawn more and more attention. On the other hand, in order to reduce production costs, the thickness of silicon wafers used in solar cells is usually less than 200 μm , resulting in high fragment rate of silicon wafers during manufacture. Therefore, improving the mechanical strength of silicon wafers has become particularly vital as increasingly gravitational or thermal stresses might cause warpages or cracks of wafers in the manufacturing process [2, 3].

With the development of modern aviation industry and nuclear industry, silicon-based electronic components and integrated circuits are frequently used in irradiation environment. When silicon materials and silicon-based devices are bombarded with high energy particles, silicon atoms will deviate from their original positions and form point defects [4, 5], which affect the electrical and mechanical properties of silicon. Because the diffusion rate of interstitial silicon atoms is much higher than that of vacancies, interstitial silicon atoms tend to diffuse out of the surface, and a large number of vacancies remain in silicon [6]. The mobile vacancies easily interact with unavoidable oxygen impurities in CZ silicon and form vacancy

oxygen (VO) complex [7]. In the subsequent thermal treatment, VO complex prefers to trap the mobile vacancies or interstitial oxygen, forming V_mO_n complexes such as V_2O , VO_2 and VO_3 [8]. The electrical properties of such V-O complexes in silicon have been extensively studied for years [9-11]. However, the effect of vacancy defects (mostly V-O complexes) on the mechanical properties of silicon has not been fully understood.

As we know, a number of studies have investigated the impacts of external impurities on the mechanical strength of CZ silicon [12-16]. Chen *et al* [13] have reported that germanium doping can block the mobilization of dislocations in CZ silicon, since the germanium-related complexes facilitate the generation of small and high density oxygen precipitates. Yang *et al* [14, 15] have reported that nitrogen doping can increase the activation energy of the dislocation motion, thus enhances the mechanical strength of CZ silicon. In addition, other impurities such as carbon and nickel have been implanted into silicon to improve the mechanical strength of silicon due to the increased bond energy between the impurities and silicon atoms [16].

In this work, neutron irradiation is carried out on CZ silicon to form point defects and then the mechanical properties of irradiated silicon have been investigated by means of nanoindentation measurements. The evolutions of V-O complexes in NICZ silicon during annealing have been characterized by Fourier transform infrared spectroscopy (FTIR) measurements. Micro-Raman spectroscopy measurements are used for phase transform analysis. The underlying mechanisms also have been discussed.

Experimental

The n-type, (100) oriented 4 inch CZ silicon wafers with a thickness of 2 mm were used in this study. The resistivity is $\sim 10 \Omega \cdot \text{cm}$, measured by the four probe method, and the interstitial oxygen concentration is $9.3 \times 10^{17} \text{cm}^{-3}$, determined by the FTIR technique at room temperature (RT) with a calibration coefficient of $3.14 \times 10^{17} \text{cm}^{-2}$. The wafers were cutted into $20 \text{ mm} \times 20 \text{ mm}$ pieces, and then they were divided into two groups. One was subjected to neutron irradiation in a fast neutron reactor at RT with a dose of $5 \times 10^{17} \text{cm}^{-2}$, while the another was conventional CZ silicon as a reference. After irradiation, all the samples were subjected to chemical mechanical polishing, followed by standard RCA cleaning and dipping into the diluted HF solution for 3 minutes to remove the native oxide from the silicon surfaces. Then, the irradiated samples were isochronally annealed in argon atmosphere in the temperature range of 250-650 °C for 20 min. The evolutions of V-O complexes in the samples during the annealing processes were monitored by FTIR at RT.

Nanoindentation tests were carried out at RT using a nanoindenter (Nanoindenter G200, USA) equipped with a Berkovich diamond indenter. A maximum load P_{max} of 10 mN was performed with the holding time of 30 s to minimize the time-dependent plastic effect, and the constant loading/unloading rate was 0.05 mN/s. In this measurement, the $\langle 110 \rangle$ direction of the samples was parallel to one face of the indenter. Each sample was indented at 7 points to check reproducibility of the data. The phase transitions induced by indentation in the specimens were investigated using a micro-Raman spectroscopy (Renishaw, UK) with the excitation wavelength of 532

nm from an Ar^+ laser. The laser beam size was about 4 μm , and the laser power was 20 mW with an integration time of 10 s. Raman spectra were acquired on indentations, which were produced by a Vickers microindenter with a load of 10 g and a loading/unloading rate of 30 mN/s.

Results and discussion

Figure 1 shows two typical selected load-displacement (P-h) curves for the CZ and NICZ silicon specimens, respectively. As can be seen, the CZ and NICZ silicon show similar P-h curves with continuous loading/unloading segments, associated with pop-out events in both specimens during the unloading process. Jang *et al* [17] demonstrated that no cracks were formed when the indentation P_{max} was lower than 80 mN. Hence, there are no cracks introduced in the indentation region and dislocations are difficult to generate when the P_{max} is 10 mN in our investigation. The samples only undergo elastic and plastic deformation during loading [18]. The plastic deformation is dominated by the phase transition from the cubic diamond phase (Si-I) to the metallic β -Sn structure phase (Si-II) during the loading process [19]. The unloading curves depend on loading/unloading rate and P_{max} . In general, slower loading/unloading rate and higher P_{max} result in the Si-II phase transforming to body centered cubic phase (Si-III) and rhombohedral structure phase (Si-XII), consequently pop-out in the unloading segment appears. While at faster rates and lower loads, the Si-II phase can further transform to amorphous phase (a-Si), in this case, elbows are often observed [20]. For the P_{max} of 10 mN and unloading rate of 0.05 mN/s, pop-out effects generally occur in CZ silicon [17, 20]. In this work, pop-out effects are also

observed in both samples, which coincide with the results reported before. Moreover, it can be clearly seen from Figure 1 that the maximum indentation displacement in the CZ silicon is about 16 nm deeper than that in NICZ silicon, which means that the hardness of the NICZ silicon is larger than that of the CZ silicon. Therefore, we speculate that neutron irradiation has an influence on the mechanical properties of CZ silicon.

The values of hardness can be determined from the following formula,

$$H = \frac{P_{max}}{A} \quad (1)$$

where H is the hardness, P_{max} is the maximum load and A is the projected area of contact at maximum load.

The Young's modulus of the specimens can be calculated using the Oliver-Pharr method [21] through the following formula,

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

where E_r is relative modulus, which can be extracted from the unloading-displacement data. E and ν are the Young's modulus and Poisson's ratio for the specimen, E_i and ν_i are those for the indenter, respectively. For the diamond indenter, $E_i = 1141$ GPa, $\nu_i = 0.07$, and for silicon, $\nu = 0.3$ [21].

The hardness of the CZ and NICZ silicon samples are calculated to be 10.29 ± 0.29 GPa and 11.58 ± 0.24 GPa, respectively, as illustrated in Figure 2. Note that the hardness of the CZ silicon is consistent with the reported values [22]. The Young's modulus of the CZ and NICZ silicon samples are calculated to be 190.69 ± 6.03 GPa

and 185.52 ± 6.43 GPa, respectively. The results demonstrate that the hardness of NICZ samples obviously increases after neutron irradiation, by a percentage of ~13%. Meanwhile, the Young's modulus of NICZ samples slightly decreases.

The Young's modulus is a result of the interatomic forces between the constituent atoms [1]. Under the condition of neutron irradiation, a high concentration of point defects are generated in silicon [5]. Previous reports have demonstrated that Young's modulus of silicon decreases with increasing point defect concentration based on theoretical calculation, and moreover, its changes are confined to a surprisingly small range [23, 24]. The simulation result is in good agreement with the slightly reduced Young's modulus in our experimental results, and we thus believe that it is mainly attributed to the vacancy defects caused by irradiation which reduce the bonding forces between silicon atoms to some extent. On the other hand, the hardness of the NICZ samples significantly increases compared with the CZ samples. It is now generally accepted that the overall hardness is determined by the phase transformations in silicon [25]. As the phase transition often occurs in the process of nanoindentation [26, 27], it is thus considered that the phase transition may be the reason for the increase in hardness after neutron irradiation. However, the nanoindentation region is too small to measure the silicon phase transition directly by means of micro-Raman technique. Microindentation induces similar phase transition behaviors with nanoindentation during loading [28], which can be applied to analyze the phase transformation and hardness changes in CZ and NICZ silicon as follows.

Figure 3a shows the Raman spectra for undeformed region of CZ and NICZ

silicon. Both specimens exhibit a sharp peak at 520 cm^{-1} corresponding to the Si-I phase in the Raman spectra [29]. The intensity of Si-I phase of NICZ silicon is a little smaller than that of CZ silicon. The irradiation-induced reduction of crystalline phase intensity was also observed in previous work in neutron irradiated silicon [30]. Note that the specimens have undergone polishing process, thus the possible amorphization close to the surface cannot be observed. As can be seen in Figure 3b, with loading of microindentation, the characteristic Raman peaks of the Si-I phase shift to 522 cm^{-1} because of the residual compressive stresses. Besides, there appear three broad peaks around $160, 300, 470\text{ cm}^{-1}$ corresponding to the characteristic Raman peaks of the a-Si phase [31-33]. More importantly, the peaks of the a-Si phase in the NICZ silicon are stronger than those in the CZ silicon, while the Si-I phase peak of the former is much weaker than the latter.

The phase transition often occurs during microindentation in the form of Si-I \rightarrow Si-II \rightarrow a-Si [18, 27]. Youssef *et al* [26] have reported that the transformation of Si-I phase to Si-II phase may be the cause of variation in the hardness of the CZ silicon. The Si-II phase generated during the indentation test is a metastable phase, which converts into the a-Si phase very quickly when the indenter is withdrawn. Though the existence of Si-II phase cannot be directly observed, the relative content of Si-II phase can be estimated by analyzing the Raman peak of a-Si phase. The intensity of the a-Si peak at 470 cm^{-1} of the NICZ silicon is much higher than that of the CZ silicon, indicating the formation of more a-Si phase in the NICZ silicon after indentation. Therefore, it is inferred that more Si-II phase is generated in the NICZ silicon due to

the transitions of Si-I \rightarrow Si-II \rightarrow a-Si. Si-II phase has a higher hardness than Si-I phase [28], therefore the NICZ silicon show a higher hardness than the CZ silicon.

The neutron irradiation can introduce a large number of vacancies, which will further transform into V-O complexes in CZ silicon during subsequent thermal treatment [4]. The generation of vacancy defects causes lattice distortion and higher free energy around the vacancy defects, leading to an increasing driving force of phase transformation [34, 35]. This may promote the nucleation of a high-pressure phase, i. e., facilitate the phase transition from the Si-I phase to the Si-II phase in the NICZ silicon during indentation, thereby enhances the hardness of silicon. Previous studies have shown that the introduction of impurities affect the phase transformation behavior of silicon. Zeng *et al* [31] have confirmed that germanium doping promotes phase transition from the Si-I phase to the stiffer Si-II phase, thereby increases the hardness of CZ silicon under indentation. In order to verify the above conjecture, isochronal anneals were further performed to modulate the concentration of vacancy defects in NICZ silicon, followed by the nanoindentation tests to obtain the hardness of the NICZ silicon.

Figure 4 shows FTIR spectra for NICZ silicon after isochronal anneals in the temperature range of 250-650 °C for 20 min. FTIR is the most powerful characterization technique to investigate the vacancy defects in silicon, and the IR absorption bands related to V_mO_n complexes are usually observed in the range of 800-1100 cm^{-1} [36-39]. The 830 cm^{-1} band originates from VO complex, while the 889 cm^{-1} band corresponds to the VO_2 complex [36]. These V-O complexes are

formed by interstitial oxygen (O_i) capturing the mobile vacancies caused by neutron irradiation [37]. It can be obviously seen from Fig. 4 that only the VO complex peak appears in the as-irradiated sample. After annealing at 250 °C, the intensity of VO complex continues to increase as a result of capture of more vacancies by O_i . With increasing temperature, the VO complex is decomposed into individual vacancy and O_i by the reaction of $VO \rightarrow V + O_i$. Simultaneously, the VO_2 complex is formed by the reaction of $VO + O_i \rightarrow VO_2$ [40]. Therefore, after annealing at 450 °C, the VO complex band completely vanishes, meanwhile the VO_2 complex is observed in the NICZ samples. When the annealing temperature increases up to 650 °C, both the peaks of VO and VO_2 complexes disappear. It is believed that, the VO and VO_2 complexes will form more complicated V_mO_n complexes [41], while the rest part of vacancies could recombine with interstitial silicon atoms or diffuse out of the silicon surface, thereby reducing the amount of vacancies in silicon.

Figure 5 shows the hardness variation of the NICZ silicon after isochronal anneals. It can be seen that, the hardness of the NICZ silicon decreases gradually from 11.58 ± 0.24 GPa to 10.06 ± 0.28 GPa with increasing annealing temperature from 250 to 650 °C. In other words, the hardness of the samples decreases with the decrease of vacancy defect concentration. Note that the hardness almost recovers to the original value without irradiation after annealing at 650 °C. It is evident that with the reduction of the vacancy concentration during annealing processes, the silicon lattice is almost restored to the original arrangement, which may mitigate the phase transition from Si-I phase to the stiffer Si-II phase under indentation and thus result in the reduction

of the hardness of the NICZ silicon.

Conclusion

We have studied the effects of vacancy defects on the mechanical properties in NICZ silicon. The NICZ silicon has higher hardness (~13% higher) in average compared with CZ silicon. It is found that the vacancy defects induced by neutron irradiation, promote the phase transition from Si-I phase to the stiffer Si-II phase, resulting in an improvement in the hardness of the NICZ silicon. After isochronal anneals in the temperature range of 250-650 °C, the concentration of vacancies decreases in the forms of annihilation and transforming into more complex defects, leading to a decrease of the hardness of NICZ silicon to the original level. In addition, the NICZ silicon has slightly lower Young's modulus in average, which could be due to the reduced bonding forces between silicon atoms induced by the vacancy defects.

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Figure captions

Figure 1 Nanoindentation load-displacement (P-h) curves of the CZ and NICZ silicon with characteristic event ("pop-out") in the unloading segment, obtained at a constant loading/unloading rate of 0.05 mN/s and maximum load P_{\max} of 10 mN.

Figure 2 Histograms of (a) hardness and (b) Young's modulus comparisons for CZ and NICZ silicon.

Figure 3 Raman spectra taken from CZ and NICZ silicon on (a) pristine material outside the impression and (b) Vickers impressions. The indentations were produced by a Vickers microindenter with a load of 10 g and a loading/unloading rate of 30 mN/s.

Figure 4 Room temperature FTIR absorption spectra of the NICZ silicon subjected to isochronal anneals in argon atmosphere in the temperature range of 250-650 °C for 20 min.

Figure 5 Variation of the hardness of the NICZ silicon as a function of the annealing temperature. The samples subjected to isochronal anneals in argon atmosphere in the temperature range of 250-650 °C for 20 min. Each error bar represents the maximum deviation.

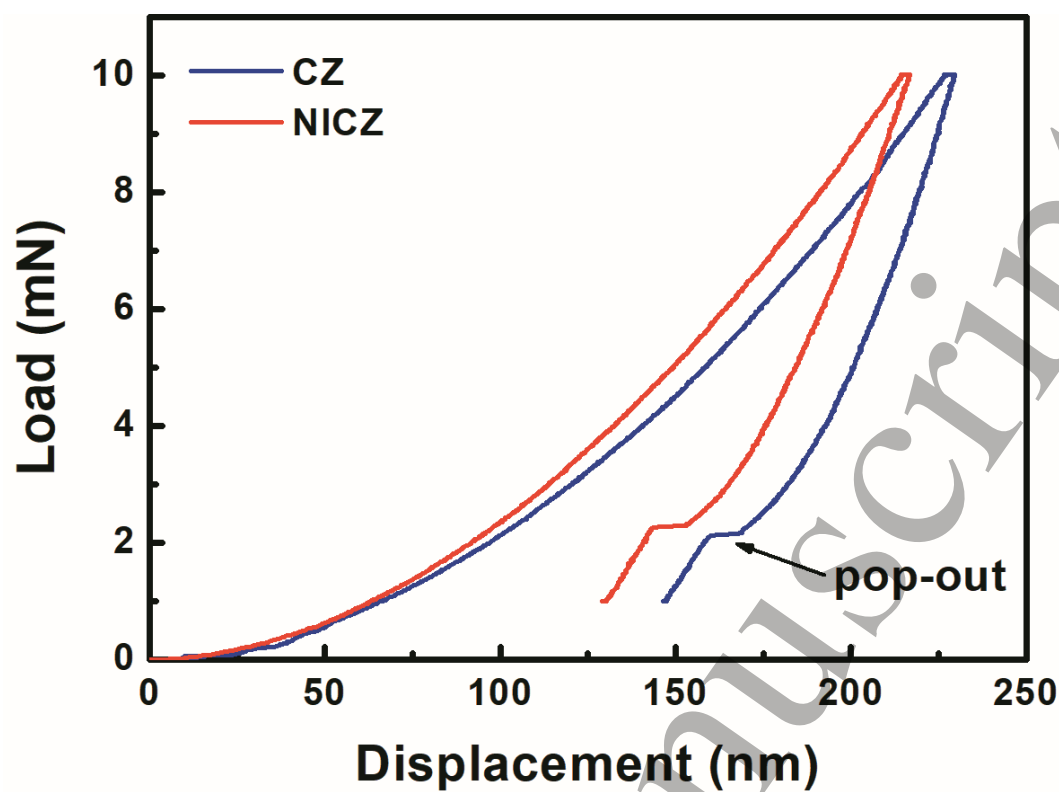


Figure 1

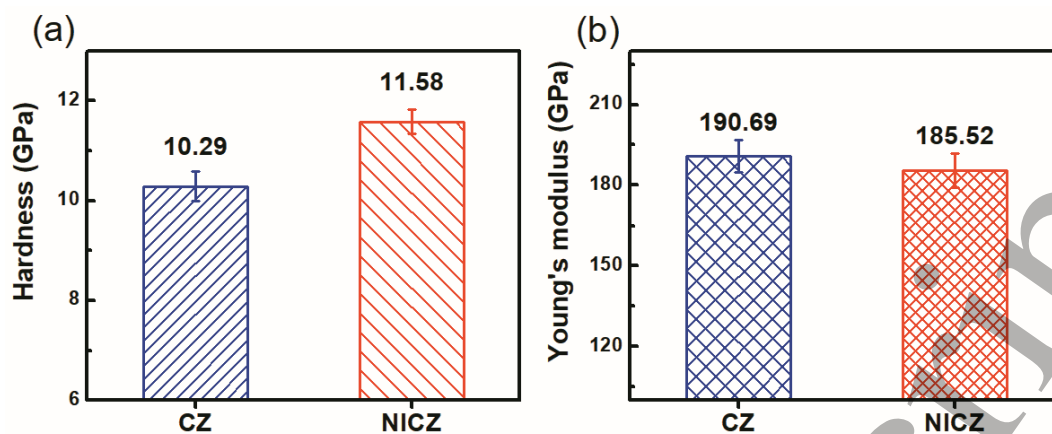


Figure 2

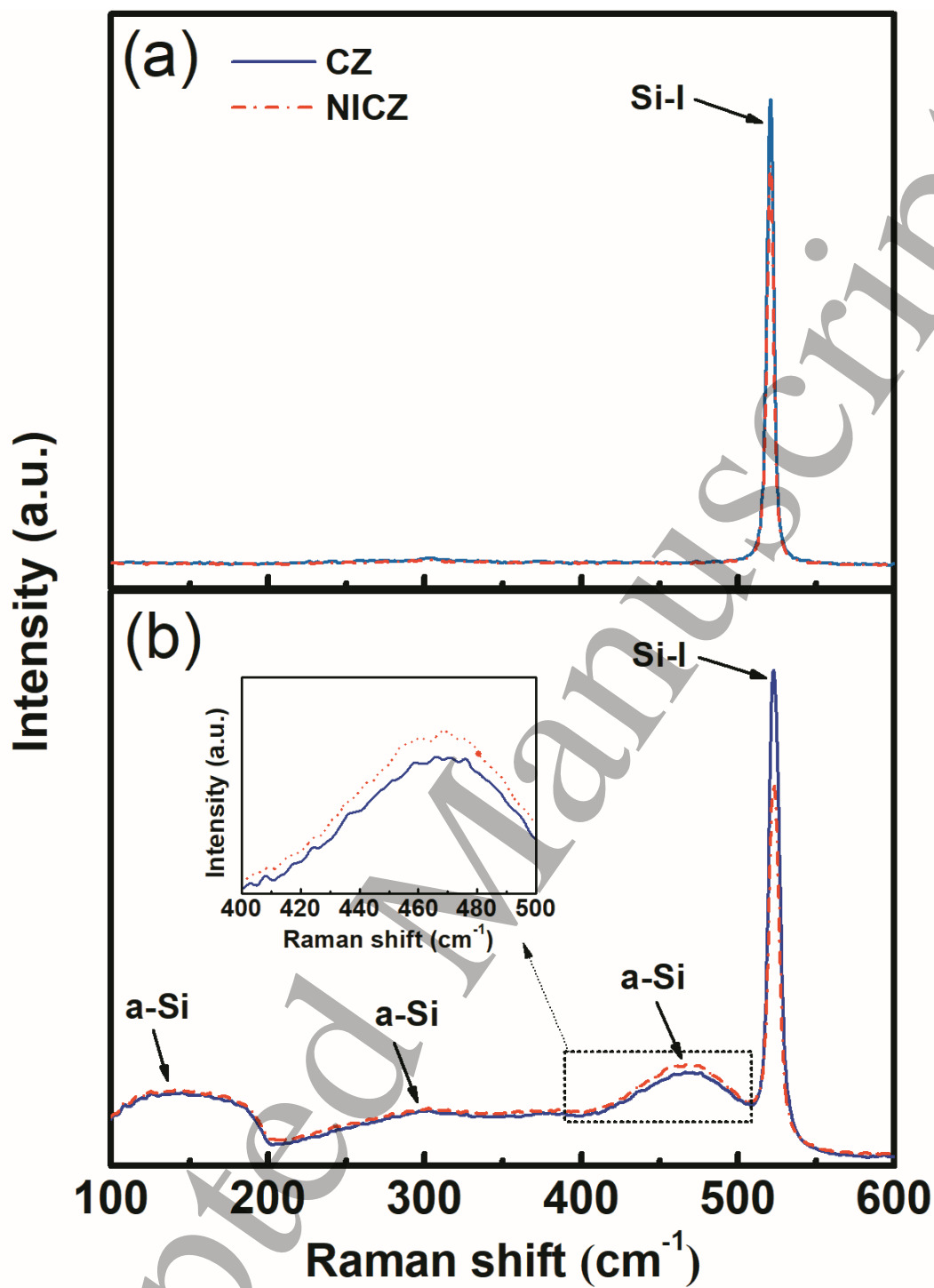


Figure 3

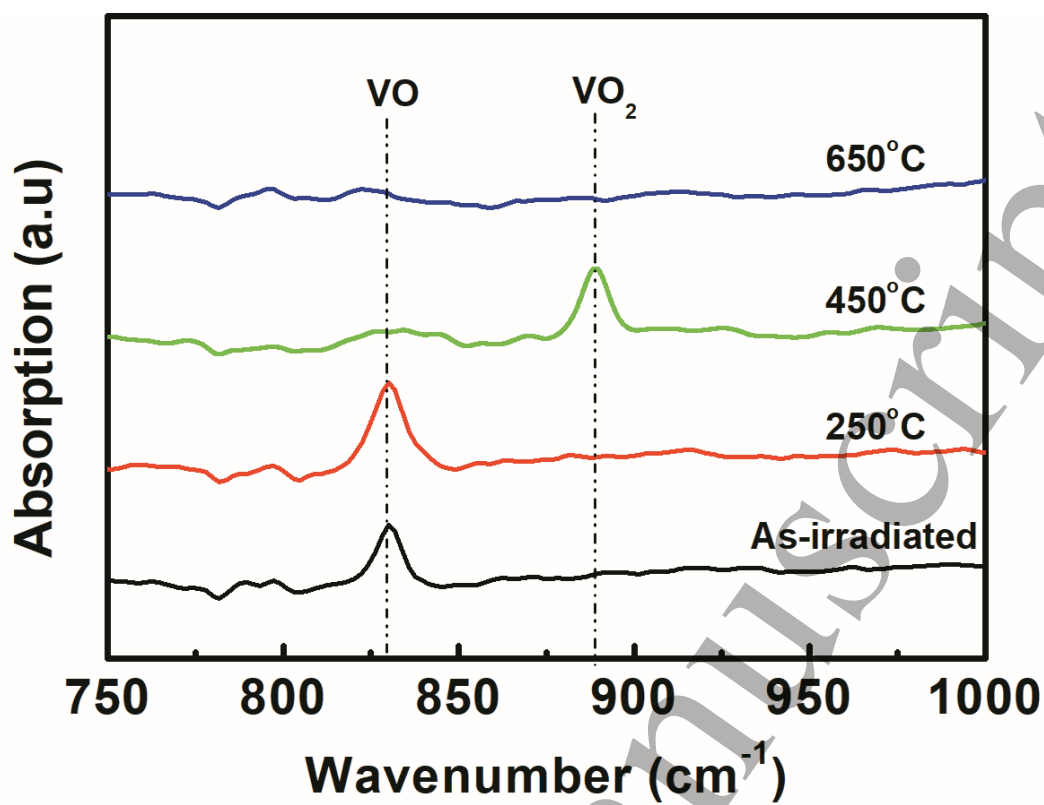


Figure 4

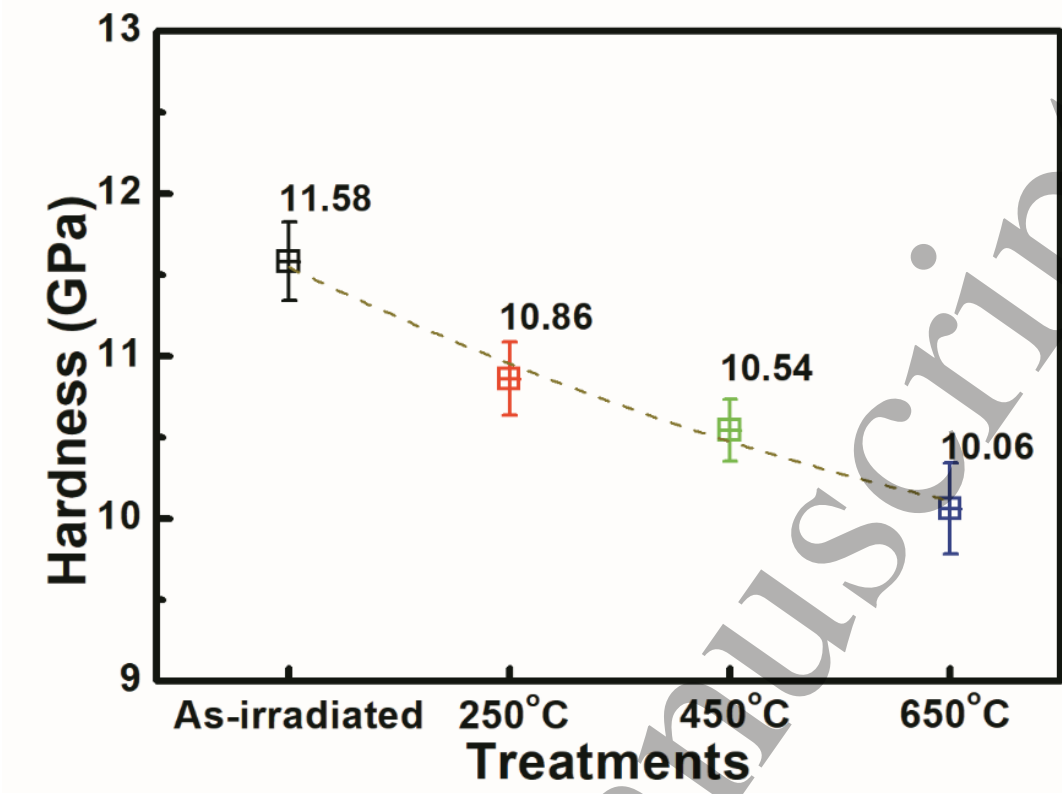


Figure 5