Effects of nitrogen doping on vacancy-oxygen complexes in neutron irradiated Czochralski silicon

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ABSTRACT

We have investigated the effect of nitrogen doping on the evolution of vacancy-oxygen (V-O) complexes in neutron irradiated Czochralski (CZ) silicon. During isothermal anneals in the temperature range of 290–330 °C, it is found that both the annihilation rate of VO and generation rate of VO_2 are obviously modified with nitrogen doping. Correspondingly, the activation energies for VO annihilation and VO_2 generation are 1.84 and 1.23 eV, both smaller (~ 0.24 eV) than those of the conventional CZ silicon. Moreover, the critical temperatures for total disappearance of VO and VO_2 peaks decrease in nitrogen doped CZ silicon, which means that the conversion processes of VO to VO_2 and VO_2 to VO_3 are promoted, respectively. It is suggested that the nitrogen doping in CZ silicon which introduces a tensile stress enhances the diffusion of vacancy and VO complex, promoting the conversion of V-O complexes.

1. Introduction

Czochraski (CZ) silicon is a dominating material for current photovoltaic and microelectronic industry [1–4]. During the growth of CZ silicon, point defects are unavoidable which play an important role in the properties of silicon wafers. Specially, more point defects are produced in neutron or electron irradiation circumstance. Vacancies and self-interstitials are formed simultaneously during particle irradiation, while most of them are annihilated through recombination reaction and the rest part of them prefer to form different complexes with impurity atoms. Oxygen is an important impurity located at interstitial sites in the silicon lattice, with a concentration of $\sim 10^{18} \, \mathrm{cm}^{-3}$ in CZ silicon. Vacancies are easily trapped by oxygen atoms, leading to a formation of vacancy-oxygen (V-O) complexes. The VO complex is called A-centre [5–8], which introduces an acceptor lever at E_c - 0.17 eV in the energy gap of silicon. It will result in the reduction of minority carrier lifetime in silicon materials, detrimental to the performance of semiconductor devices [9]. Upon annealing, VO complex can combine with vacancy or interstitial oxygen to form more complicated complexes [10,11], such as V_2O, VO_2, VO_3, and so on.

The V-O complexes serve as important precursors for forming oxygen precipitates during the subsequent anneals [12–15]. Cui et al. [16,17] previously reported that the density of oxygen precipitation obviously increases in neutron irradiated CZ silicon. The formation of oxygen precipitation has gone through a series of processes, in which the conversion of V-O complexes should be given special attention. C. A. Londos et al. have symmetrically studied the conversion capability of VO to VO_2 and VO_2 to VO_3, under the impact of isovalent dopant doping (C, Ge, Sn, Pb) [18–21]. Yu et al. have investigated the kinetic process of VO to VO_2, which is affected by the Ge doping [22]. The related characteristic parameters have been quantified, and the results are important for us to understand the evolution of V-O complexes in silicon. Nitrogen is another important impurity, which is intentionally introduced into CZ silicon under nitrogen atmosphere. The nitrogen doping promotes the formation of thermal donor and oxygen precipitates [23–25], and improves the mechanical properties of silicon wafers. Moreover, the oxygen precipitates in neutron irradiated silicon are further promoted by nitrogen doping [16]. However, the effect of nitrogen doping on the kinetic process of V-O complexes in neutron irradiated CZ silicon has never been reported before.

In this work, we have studied the kinetic behaviors of V-O complexes in conventional and nitrogen doped CZ (NCZ) silicon with neutron irradiation. The evolutions of VO and VO_2 complexes are monitored by a Fourier transform infrared (FTIR) spectrometer. Both the activation energies for VO annihilation and VO_2 generation are smaller in NCZ silicon than those in conventional CZ one. Moreover, the critical temperatures for the complete conversion of VO to VO_2 and VO_2 to VO_3 decrease with nitrogen doping.

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Table 1
Neutron irradiation dose, initial interstitial oxygen concentration (O$_i$) and nitrogen density for the samples.

Sample	Neutron irradiation dose (cm^{-2})	O$_i$ (cm^{-3})	Nitrogen density (cm^{-3})
CZ	1.83×10^{13}	$\sim 9.3 \times 10^{17}$	0
NCZ	1.83×10^{13}	$\sim 9.5 \times 10^{17}$	1×10^{14}

2. Experimental details

Two n-type < 111 > CZ silicon wafers with a resistivity of ~ 10 Ω cm. One was conventional CZ and the other was NCZ, with a nitrogen concentration of $\sim 1 \times 10^{14}$ cm^{-3}. The carbon content is beyond the detection limit and is thus negligible. Both samples were subjected to 1 MeV fast neutron irradiation at room temperature (RT) with a flux of 1.83×10^{13} cm^{-2}. The parameters are summarized in Table 1. The interstitial oxygen concentrations were measured by FTIR at RT with a calibration coefficient of 3.14×10^{17} cm^{-2} (ASTM F 121-89 standard). After chemical-mechanical polishing to remove the surface saw damage and careful cleaning, the samples were subjected to isothermal anneals in argon atmosphere in the temperature range of 290–330 °C. Then, the evolution of VO and VO$_2$ complexes as a function of time was measured by FTIR spectrometer, which was performed on the annealed samples at RT with a resolution of 1 cm^{-1}. The absorption coefficients from VO complex and from VO$_2$ complex were both obtained by integrating the IR peaks after separating the overlapped bands by means of Lorentzian profile fitting [20]. Furthermore, the CZ and NCZ samples were isochronally annealed in argon atmosphere in the temperature range of 200–300 °C with 20 °C as an increment , followed by 300–620 °C with 10 °C as an increment. Each sample was subjected to the thermal anneals with a duration time of 20 min. After cooling down, the samples were measured with FTIR at RT to monitor the changes of peaks of V-O complexes.

3. Results and discussions

Fig. 1 shows typical absorption spectra at RT of neutron irradiated CZ silicon before and after annealing at 290 °C. Only a peak at 830 cm^{-1} appears in the irradiated CZ sample before annealing, which is originated from the VO complex [26]. After annealing at 290 °C for 6 h, the intensity of the band at 830 cm^{-1} becomes weaken and a new band at 889 cm^{-1} from VO$_2$ complex appears. The main reason should
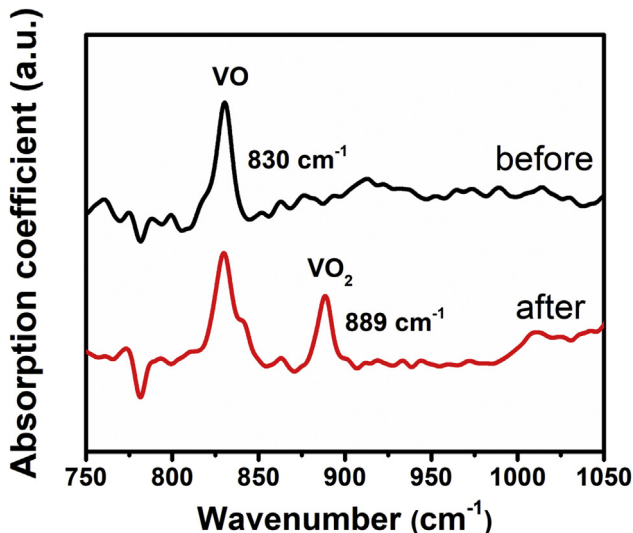

Fig. 1. Absorption spectra of neutron irradiated CZ silicon before and after annealing at 290 °C for 6 h.

be ascribed that the VO complex is dissociated into individual vacancy and interstitial oxygen (O$_i$) by the reaction of VO→V + O$_i$, and meanwhile, the VO$_2$ complex is formed by VO complex and O$_i$ with the reaction of VO + O$_i$→VO$_2$ [22]. Note that Fig. 1 illustrates a schematic conversion between VO and VO$_2$ complexes, the thermally activated processes of VO annihilation and VO$_2$ generation need to be specified, especially under the effect of nitrogen doping in irradiated CZ silicon.

Fig. 2 shows the evolution of VO complex as a function of isothermal anneal time in the temperature range of 290–330 °C for the neutron irradiated CZ and NCZ silicon. It can be obviously seen that the absorption intensity of VO complex in CZ silicon decreases with the increase of anneal time, and it reaches a saturated value in the time scales of several hundreds of minutes (Fig. 2a). Moreover, the higher anneal temperature is, the more quickly VO intensity decreases. The similar trend is observed in NCZ sample (Fig. 2b). When the isothermal anneal temperature is 330 °C, the saturated values are almost the same in both samples. Note that the saturated value mentioned here should be the difference between the initial VO complex value and the saturated one. However, the annihilation rates of VO complex in such two samples are different. In the temperature range of 290–300 °C, the saturation occurs at earlier time in NCZ silicon. On the contrary, the intensity of VO complex from CZ silicon reaches saturation first at the larger anneal temperatures (320–330 °C). It indicates that the annihilation rate of VO complex in NCZ-Si is higher at the smaller anneal temperatures, whereas it is lower at the higher temperatures. Thus, we infer that nitrogen doping affects the kinetic process of VO annihilation in CZ silicon.

Fig. 3 shows the evolution of VO$_2$ with the isothermal anneal time for the neutron irradiated CZ and NCZ silicon in the same temperature range. For CZ and NCZ samples, the absorption intensity of VO$_2$ complex increases with the increase of anneals time, and it gradually reaches a saturated value. As anneals temperature increases, the VO$_2$ intensity increases more quickly. It should be noticed that nitrogen doping also has an influence on the generation process of VO$_2$ complex by comparing Fig. 3a and b. In the isothermal anneal temperature range of 290–310 °C, the generation of VO$_2$ complex in NCZ silicon is faster than that in CZ sample, and the saturated values in NCZ silicon are larger than those in CZ one. In fact, nitrogen, as an impurity with a smaller tetrahedral radius than silicon, similar to the carbon atoms in silicon, can induce a tensile stress in silicon lattice [27]. This stress should affect the kinetic processes of both VO annihilation and VO$_2$ generation.

The annihilation rate of VO complex ($R_{VO,ann}$) during annealing can be obtained as [28],

$$I_{VO}(t, T) = I_{VO}(t = 0)\exp(-R_{VO,ann}t) \qquad (1)$$

and the generation rate of VO$_2$ complex ($R_{VO_2,gen}$) can be expressed as,

$$I_{VO_2}(t, T) = I_{VO_2}(t \to \infty)\left[1 - \exp\left(-R_{VO_2,gen}t\right)\right] \qquad (2)$$

where $I_{VO}(t, T)$ and $I_{VO_2}(t, T)$ are the absorption intensities of VO and VO$_2$ complexes at the absolute temperature (T) for an isothermal anneal time of t, respectively. $I_{VO}(t = 0)$ and $I_{VO_2}(t \to \infty)$ are the absorption intensities of initial VO and saturated VO$_2$ complex, respectively. The corresponding $R_{VO,ann}$ and $R_{VO_2,gen}$ at different anneal temperatures are obtained by fitting eqs. (1) and (2) to the measured data in Figs. 2 and 3 for CZ and NCZ silicon, respectively.

Fig. 4 shows the Arrhenius plots of R_{ann} for VO annihilation and R_{gen} for VO$_2$ generation in the neutron irradiated CZ and NCZ silicon as a function of inverse temperature (1/T). Obtaining $R_{VO,ann}$ and $R_{VO_2,gen}$ at different temperatures allows the determination of the activation energies of VO annihilation ($E_{VO,ann}$) and VO$_2$ generation ($E_{VO_2,gen}$) using the Arrhenius equation,

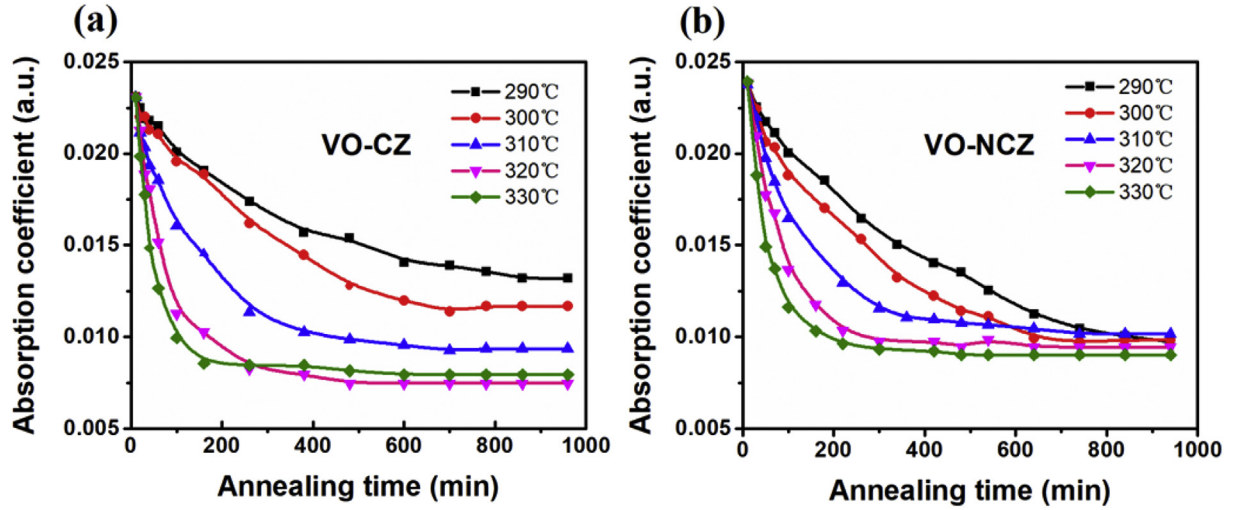$$R_{VO,ann} = k_{VO,ann} \exp\left(-\frac{E_{VO,ann}}{k_B T}\right) \qquad (3)$$

Fig. 2. The evolution of VO with the isothermal anneal time for the neutron irradiated CZ (a) and NCZ (b) silicon.

$$R_{VO2,gen} = k_{VO2,gen} \exp\left(-\frac{E_{VO2,gen}}{k_B T}\right)$$

(4)

where k_B is the Boltzman's constant, $k_{VO,ann}$ and $k_{VO2,gen}$ are the pre-exponential factors of VO annihilation and VO_2 generation processes, respectively. Based on the Arrhenius fittings, the $E_{VO,ann}$ are 2.08 and 1.84 eV for CZ and NCZ silicon, respectively. Likewise, the $E_{VO2,gen}$ are 1.47 and 1.23 eV for CZ and NCZ samples, respectively. It is believed that nitrogen doping reduces the energy barriers for VO annihilation and VO_2 generation. Besides, it is found that the $k_{VO,ann}$ are 3.78×10^{15} and 2.96×10^{13} s^{-1} for CZ and NCZ silicon, and the $k_{VO2,gen}$ are 3.11×10^{10} and 2.45×10^8 s^{-1} for CZ and NCZ silicon, respectively. The pre-exponential factors of both VO annihilation and VO_2 generation have been reduced by two orders of magnitude with nitrogen doping.

For the annihilation of VO complex by the reaction of VO→V + O_i, the $E_{VO,ann}$ approaches to the sum of the binding energy of vacancy and interstitial oxygen and the migration energy of the vacancy. Usually, the binding energy is hardly affected by external atom doping. Thus, the decreased $E_{VO,ann}$ in NCZ indicates that nitrogen doping reduces the migration energy of the vacancy. On the other hand, for the generation of VO_2 complex by the reaction of VO + O_i→VO_2, we suggest the $E_{VO2,gen}$ equals to the migration energy of VO complex, which is similar to that of the generation of B-O complexes [29]. As refs 1 and 20, when

the atomic radius is much larger than silicon atom, for instance, Ge, Sn, Pb atoms, the evolution of the VO and VO_2 complexes is suppressed. Besides, the hydrostatic pressure in silicon can affect self-diffusion and dopant diffusivity [30–32]. Hence, the higher compressive strain around Ge, Sn, Pb, leads to a retardation of vacancy diffusion. On the contrast, the nitrogen or carbon atoms can introduce a tensile stress into silicon lattice , promoting the diffusion of vacancy and VO complex. As a result, nitrogen doping in CZ reduces energy barriers and pre-exponential factors in the conversion process of VO to VO_2.

Fig. 5 shows the evolution of VO and VO_2 complexes for isochronal anneals as a function of the anneal temperature in the range of 200–620 °C for the neutron irradiated CZ and NCZ silicon. In the isochronal anneal temperature range of 300–400 °C, the absorption intensity of VO complex decreases and it finally reduces close to zero. While in the isochronal anneal temperature range of 300–600 °C, the absorption intensity of VO_2 complex increases at first, and it comes to the maximum value at ∼ 450 °C, afterwards it decreases. At about 370 °C, there is a change in the generation rate of VO_2 complex in both Fig. 5a and b. We suggest that the intensity of VO complex has decreased significantly, even weaker than that of VO_2 at this temperature. It indicates that the process of VO + O_i→VO_2 becomes less effective. Interestingly, when the isochronal anneal temperature is about 400 °C, the VO complex stabilizes in each minimum value, and the VO_2 complex continues to increase for some temperature interval. We infer that
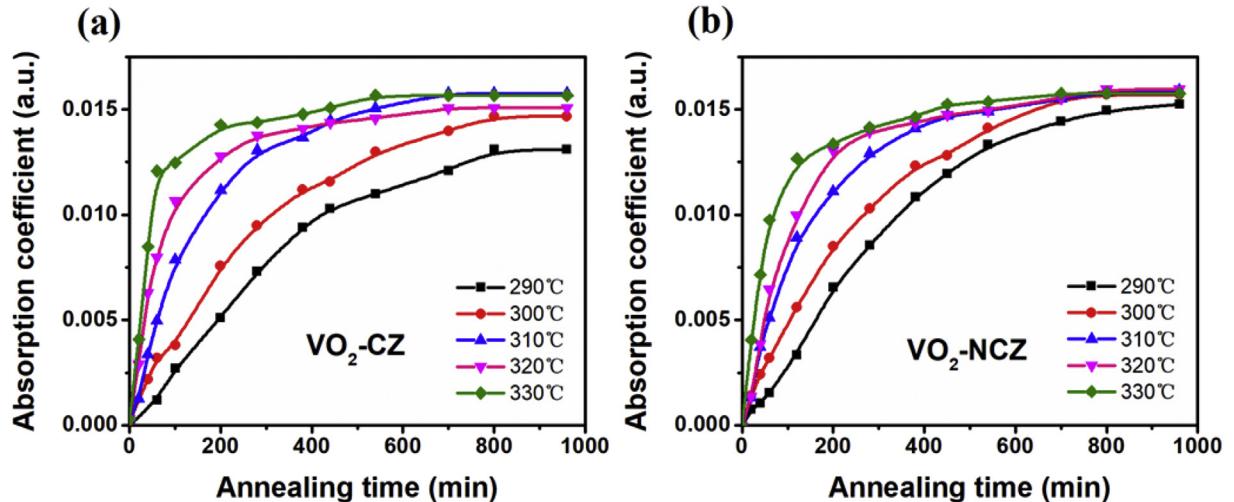

Fig. 3. The evolution of VO_2 with the isothermal anneal time for the neutron irradiated CZ (a) and NCZ (b) silicon.
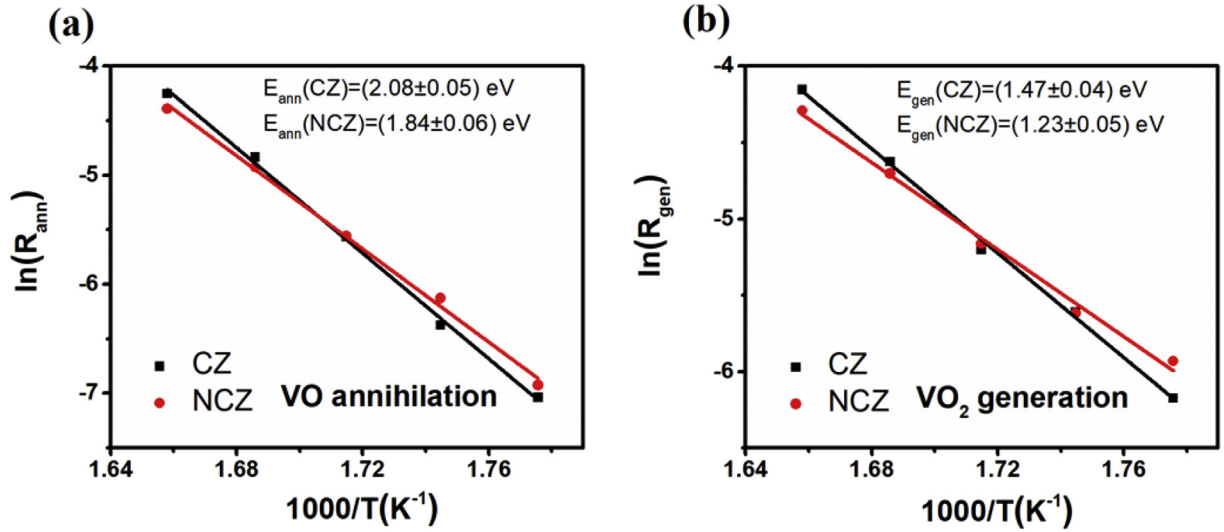
Fig. 4. Arrhenius plots of R_{ann} for VO annihilation (a) and R_{gen} for VO_2 generation (b) in the neutron irradiated CZ and NCZ silicon as a function of inverse temperature ($1/T$).

there might be existence of intermediate phase for the evolution of VO to VO_2 complex [14]. When the VO complex disappears completely, the metastable intermediate phase still exists, which converts into VO_2 and the intensity of VO_2 continues to increase as the isochronal temperature increases.

More importantly, we notice that the critical temperature points at which the bands of VO and VO_2 complexes totally disappeared in CZ and NCZ silicon are different. The critical temperatures for the complete disappearance of VO complex are 410 and 390 °C for CZ and NCZ silicon, respectively. Similarly, the critical values for the disappearance of VO_2 complex are 580 and 560 °C for CZ and NCZ silicon, respectively. Thus, it indicates that nitrogen doping promotes the conversion process of $VO + O_i \rightarrow VO_2$ in the temperature range of 300–400 °C, also boosts the process of $VO_2 + O_i \rightarrow VO_3$ at higher temperature. This is in good agreement with above studies that nitrogen doping reduces the energy barriers and enhances the diffusion of vacancy and VO complex. The promoting conversion process of V-O complexes helps the nucleation of oxygen precipitates in nitrogen-doped CZ silicon [16].

4. Conclusions

We have demonstrated the effect of nitrogen doping on the kinetic behaviors of V-O complexes in neutron irradiated CZ silicon. The obtained activation energies of VO annihilation are 2.08 and 1.84 eV for CZ and NCZ silicon, respectively. The activation energies of VO_2 generation are 1.47 and 1.23 eV for CZ and NCZ samples, respectively. Correspondingly, the pre-exponential factors are reduced by two orders of magnitude in NCZ silicon. Besides, the critical temperatures for the complete disappearance of VO and VO_2 complexes during the isochronal anneals are lower in NCZ silicon. The results indicate that nitrogen doping which introduces a tensile stress promotes the kinetic process of V-O complexes conversion in CZ silicon.
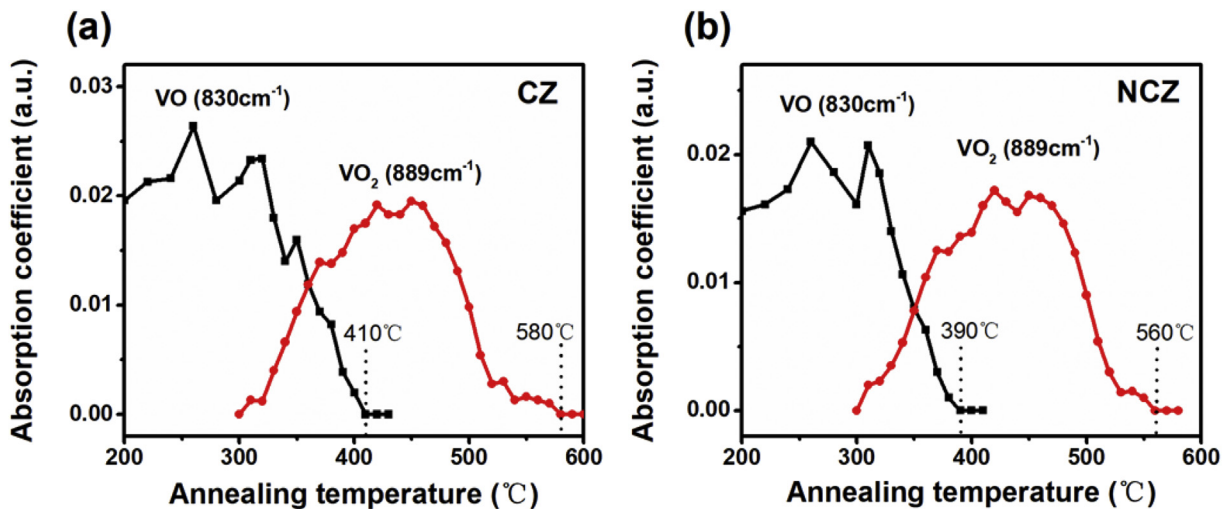
Fig. 5. The evolution of VO and VO_2 complexes for isochronal anneals of 20 min as a function of the anneal temperature in the range of 200–620 °C with 10 °C as an increment (in the temperature range of 200–300 °C with 20 °C as an increment) for the neutron irradiated CZ (a) and NCZ (b) silicon.

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