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Complementary infrared and transmission electron microscopy studies of the effect of high temperature–high pressure treatments on oxygen-related defects in irradiated silicon

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Czochralski-grown silicon samples subjected to high temperature–high pressure (HTHP) treatments in the range of 900 °C were irradiated with fast neutrons. Transmission electron microscopy measurements revealed the presence of oxygen precipitates (SiO_x) and dislocation loops. The purpose of this work is to investigate the effect of these defects on the annealing behavior of neutron-irradiated induced oxygen-related defects, mainly the VO and the VO_2 centers. To this end, infrared spectroscopy measurements were employed to monitor the conversion of the VO center ($828\,\mathrm{cm}^{-1}$) to the VO_2 center ($890\,\mathrm{cm}^{-1}$ band) during isochronal anneals. In the untreated samples this conversion occurs around 300 °C. In our studies, we found that the annealing temperature (T_{ann}) of the VO centers is lower than 300 °C. The value of T_{ann} depends on the particular HTHP pretreatment. Actually, as a result of the precipitation process silicon self-interstitials (Si_Is) are emitted and a number of them is bound at the Si/SiO_x interface. This region acts as a source of Si_Is and upon their liberation the reaction $VO+Si_I \rightarrow O_i$ is activated. The temperature at which this reaction becomes significant depends on the degree of binding of the Si_Is at the interface and the number of the Si_Is available to participate, which in turn depend on the particular HTHP pretreatment. Thus, if the reaction $VO+Si_I \rightarrow O_i$, precedes the reaction $VO+O_i \rightarrow VO_2$, the T_{ann} of the VO defect will be determined mainly by the former reaction. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1602952]

INTRODUCTION

It is well known that heat treatments of Czochralski (Cz)-Si at $T > 400\,°C$ lead to the appearance[1,2] of oxygen precipitates, rod-like defects, dislocations, stacking faults, etc. The oxygen precipitates themselves are characterized in terms of their morphology, size, and density. These parameters depend on the temperature and the time duration of the treatment. Due to the volume difference between Si and SiO_2 strain fields are created around the precipitates. Requirements for accommodation of the volume expansion and the reduction of the strain energy impose[3,4] an influx of vacancies from the bulk towards the growing precipitate particle and an outflow of silicon self-interstitials (Si_Is) to the Si/SiO_x interface. Moreover, if these Si_Is are in a oversaturated state they tend to agglomerate in order for the system to further lower its free energy. Notice, that above 850 °C dislocation loops can also be generated[5] on the precipitates in order to further relieve the strain. These dislocation loops can act as sinks for the emitted Si_Is. Generally, in heat treated silicon the Si/SiO_x interface region is considered as a potential source of Si_Is and the precipitates as potential sinks for vacancies.

The application of external hydrostatic pressure during pre-treatments at high temperatures results[6] in a stress-stimulated oxygen precipitation in the crystal. Depending on the temperature of the HP treatment all the parameters of the precipitates, i.e., their size, their number, even their morphology change. The number and the dimensions of the other accompanying structural defects also change. Apparently, due to the precipitation process the remaining number of the oxygen interstitial atoms in the Si crystal diminishes.

According to precipitate morphology three temperature regimes could be distinguished[3]: (i) 400–650 °C, (ii) 650–950 °C, and (iii) 950–1200 °C. In the middle regime mainly oxygen precipitates of platelike morphology form in the crystal. This temperature regime is very important since it

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TABLE I. The annealing temperatures (T_{ann}) of the VO defect in Si for samples subjected to various HTHP treatments prior to neutron irradiation.

Sample pretreatments			
T (°C)	P (kbars)	t (h)	T_{ann} of the VO defect
870	10^{-3}	5	(271 ± 1)
870	12	5	(281 ± 4)
960	12	5	(291 ± 3)
0	10^{-3}	0	(300 ± 1)

includes the temperature of maximum nucleation rate[7] for oxygen precipitation. Moreover, at temperatures around 900 °C thermal oxidation and diffusion are usually performed. In this sense, it would be particularly interesting to know the effect of the structural defects formed in the middle temperature regime on the properties of radiation-induced defects in Si. On the other hand, since the application of HP during the thermal treatments alters the parameters of the structural defects, it would be interesting to investigate the additional induced changes in the radiation defects.

The main defect formed upon irradiation in oxygen-rich Si is the VO center, besides divacancies. This center in the neutral charge state is characterized by an infrared (IR) band at $828\,\mathrm{cm}^{-1}$. The center is stable up to $\sim300\,°\mathrm{C}$, where it becomes mobile and converts[8] to the VO_2 center ($890\,\mathrm{cm}^{-1}$) mainly through the reaction $\mathrm{VO}+\mathrm{O}_i\rightarrow\mathrm{VO}_2$. Other reactions as $\mathrm{VO}\rightarrow\mathrm{V}+\mathrm{O}_i$, $\mathrm{VO}+\mathrm{Si}_I\rightarrow\mathrm{O}_i$, $\mathrm{VO}+\mathrm{V}\rightarrow\mathrm{V}_2\mathrm{O}$ could also take part and have been considered[9] in the literature. The presence of precipitates due to the high temperature–high pressure (HTHP) pretreatments is expected to affect the behavior of the VO defect in Si. The purpose of this article is to investigate the effect of various HTHP pretreatments in the range of 900 °C on the annealing behavior of the VO defect and its conversion to the VO_2 defect.

EXPERIMENTAL DETAILS

Cz-grown Si samples of 2 mm thickness were used in this experiment. The initial oxygen concentration in the samples was $[\mathrm{O}_i]_o\cong8.3\times10^{17}\,\mathrm{cm}^{-3}$, a value well above the critical[10] concentration for oxygen precipitation to occur upon heat treatment. The samples were subjected to thermal anneals with or without the application of high pressure at temperatures in the range of 900 °C as indicated in Table I. Afterwards, the samples were irradiated by fast neutrons at a fluence of about $10^{17}\,n/\mathrm{cm}^2$, at a temperature of $\sim50\,°\mathrm{C}$. 15 min isochronal anneals were performed after the irradiation in open furnaces with the aim to investigate the evolution of *A* centers. The evolution of these defects as well as of the oxygen interstitials was monitored by IR spectroscopy measurements performed after each stage of the annealing procedure. A JASCO-700 IR spectrometer of dispersive kind operating in the range of $400-5000\,\mathrm{cm}^{-1}$, was used. The structural defects, i.e the oxygen precipitates, the dislocation loops etc, were studied by means of transmission electron microscopy (TEM). A JEOL 200CX microscope was used operating at a voltage of 200 kV.

EXPERIMENTAL RESULTS AND DISCUSSION

A study of the effect of the oxygen precipitates and the structural defects on the behavior of radiation-induced oxygen-related defects in Cz-Si with treatments in the broad temperature range of 400–1200 °C is, in advance, exquisitely complicated due to the large number of the involved parameters. The demand to understand and clarify the above effects has led us to restrict the temperature range of the thermal treatments. We chose the middle temperature regime (650–950 °C) for two reasons: for its particular importance mentioned in the Introduction and with the intension to deal with precipitates of the same morphology, that is platelets here. Moreover, since the rod-like defects are not stable[7] above 750 °C, in order to avoid their presence, we decided to further confine the investigations at temperatures above 750 °C. To this end, we selected two temperatures at 870 and 960 °C, one lower and another higher than the characteristic temperature of 900 °C. In the same line of thought, the duration of the HTHP pretreatment was chosen to be short enough, that is 5 h, for all samples, in order to secure the same precipitate morphology. In this way, our study focuses on the effect of the magnitude and the number density of the platelet precipitates and the other structural defects, i.e., the dislocation loops, on the behavior of the centers introduced by irradiation.

Figure 1 depicts the TEM images for all samples subjected to pretreatments. Figure 2 depicts the evolution of the 828, 890, and $1106\,\mathrm{cm}^{-1}$ lines, attributed to the VO, the VO_2, and the O_i centers, respectively. Table I indicates the different pretreatments performed and the T_{ann} of the VO defect found for each sample. We immediately observe that the T_{ann} in the pretreated samples is lower than that of the untreated sample and its value depends on the particular pretreatment. In an attempt to explain these results we shall recourse to a previously used[11] model which takes into account the presence of Si_Is bound at the interface of the oxygen precipitates and the Si matrix ($\mathrm{Si}/\mathrm{SiO}_x$ interface). Actually, the degree of binding of the Si_Is at the $\mathrm{Si}/\mathrm{SiO}_x$ interface and the number of Si_Is available to react with the VO defect are different at each pretreated sample. These two factors mainly determine, in our opinion, the T_{ann} of the VO center, in the corresponding sample.

In the sample treated at (870 °C, 1 bar, 5 h) the TEM images [Fig. 1(a)] reveal the presence of small oxide precipitates. These precipitates are seen as small dark dots representing strain associated with them. No dislocations are observed. As mentioned previously the precipitates in this case are amorphous platelet SiO_x particles, with Si_Is bound at the $\mathrm{Si}/\mathrm{SiO}_x$ interface. Upon annealing, the liberation of these Si_Is to the crystal bulk activates the reaction $\mathrm{VO}+\mathrm{Si}_I\rightarrow\mathrm{O}_i$. Reasonably, the temperature at which this reaction becomes significant will affect the annealing behavior of the VO center. If the liberation of the Si_Is occurs at a lower temperature than that the VO centers become mobile, then the reaction $\mathrm{VO}+\mathrm{Si}_I\rightarrow\mathrm{O}_i$ will characterize the T_{ann} of the VO center. Apparently, this is the case for the sample pretreated at (870 °C, 1 bar, 5 h); the reaction $\mathrm{VO}+\mathrm{Si}_I\rightarrow\mathrm{O}_i$ precedes the reaction $\mathrm{VO}+\mathrm{O}_i\rightarrow\mathrm{VO}_2$. This explains the decay of the VO at a

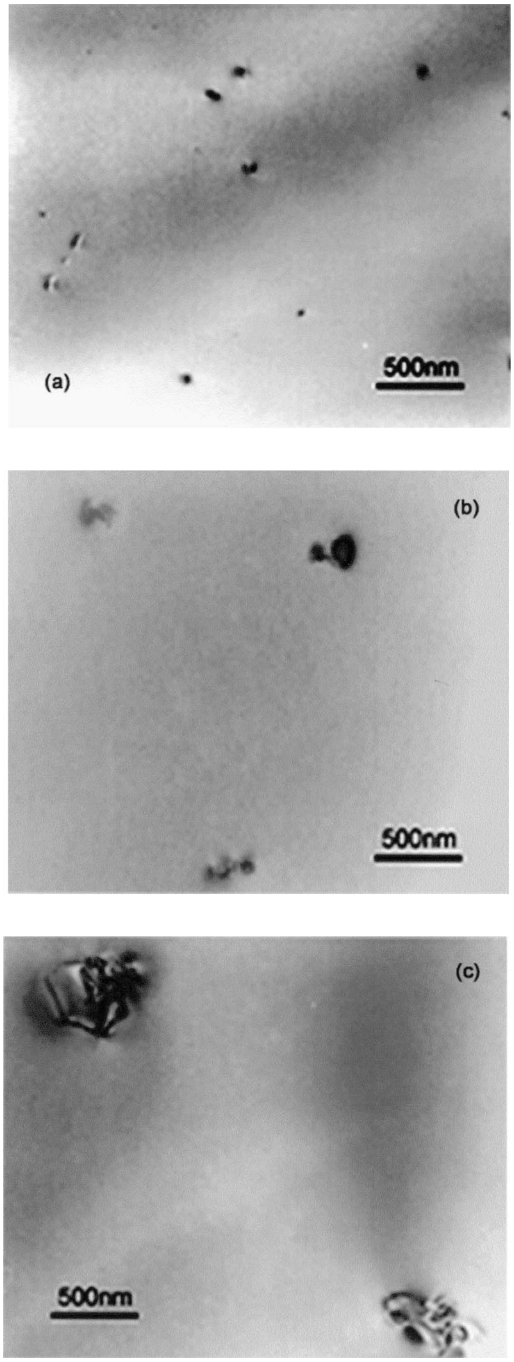

FIG. 1. TEM images of samples treated at (a) 870 °C, 1 bar, 5 h (b), 870 °C, 12 kbar, 5 h and (c), 960 °C, 12 kbar, 5 h.

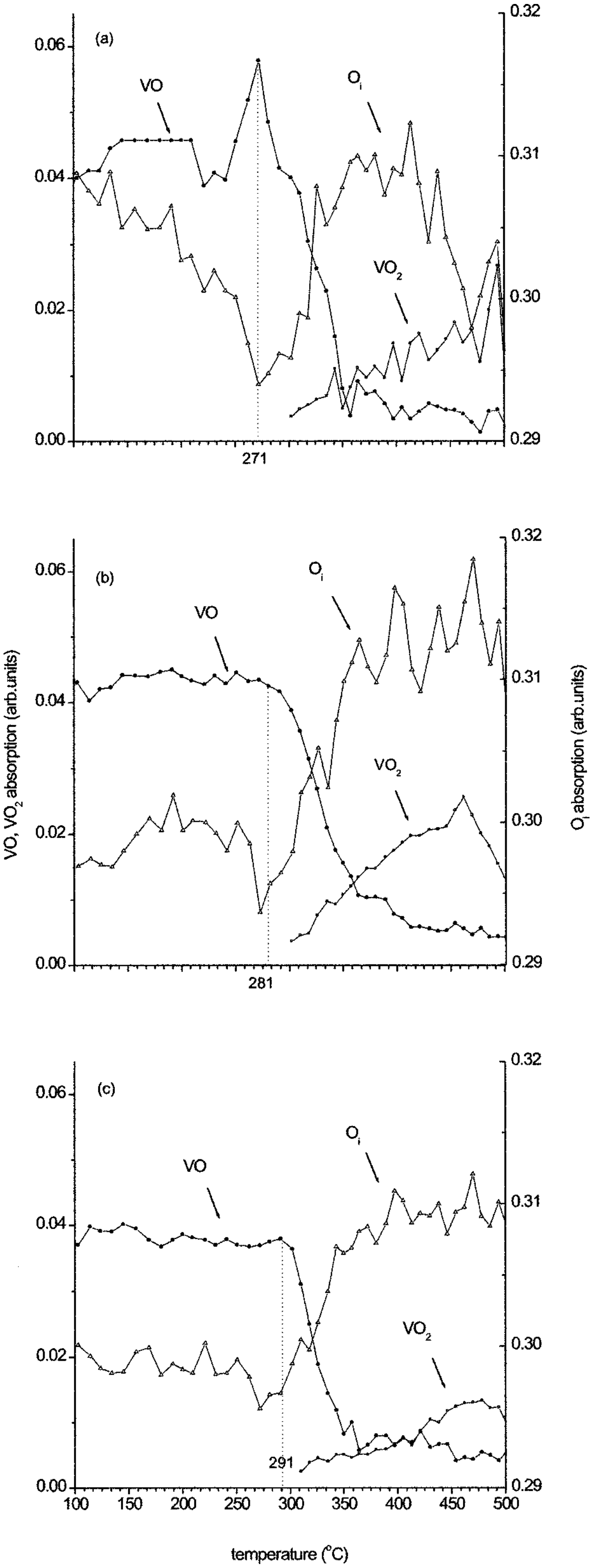

FIG. 2. 15 min isochronal annealing curves of the VO, the VO$_2$, and the O$_i$ defects of the samples depicted in Fig. 1, correspondingly.

lower temperature, i.e., at 271 °C [Fig. 2(a)] and also the observed delayed growth of the VO$_2$ defect at around 300 °C, when the reaction VO+O$_i$→VO$_2$ becomes active.

In the sample pretreated at (870 °C, 12 kbar, 5 h) the precipitates shown in the TEM images [Fig. 1(b)] are larger and also surrounded by dislocation loops. This new picture was expected[6] due to the fact that generally pressure enhances the precipitation process, manifested in our case by the formation of larger magnitude precipitates. Accordingly, larger compressive strains around the precipitates are developed. As a consequence,[12] dislocation loops form as an additional means of strain relief, besides the emission of Si$_I$s. Stacking faults are not observed in our sample. Note that, although stacking faults have been observed at 870 °C, in most studies they were not detected.[13] As we mentioned previously,[6] the precipitation process is enhanced under pressure. This means equivalently, that thermal treatments at high pressure cause the same effect with thermal treatments at atmospheric pressure but at higher temperatures, provided that the time duration of the treatment is the same. Thus, the situation of the Si_Is in the HTHP treated samples is certainly different than that of the HT treated sample. At first, the degree of binding of the Si_Is at the interface has been changed because the magnitude of the precipitates is different and the strains around them as well. The surface energy, the elastic energy and the strain energy are different.[3] Secondly, the number of the Si_I's at the interface is also different. We know[12] that with increasing temperature the ratio $C_{I(R_p)}/C_I^{\mathrm{eq}}$, where $C_{I(R_p)}$, C_I^{eq} are the Si_I concentration at the $\mathrm{Si/SiO}_x$ interface and the Si_I thermal equilibrium concentration, respectively, decreases. Since HP pretreatments at a certain temperature correspond to thermal pretreatments at a higher temperature, we conclude that the ratio $C_{I(R_p)}/C_I^{\mathrm{eq}}$ also decreases in our samples. This results in a lower concentration of Si_Is at the interface, assuming that the actual oxygen concentration, the actual Si_I concentration and the Si_I thermal equilibrium concentration in the Si matrix are the same for all the samples used. Third, another important factor that explains the results is that the dislocation loops formed are potential sinks for the Si_Is. Upon increasing the temperature of the isochronal annealing sequence, the Si_Is bound at the interface begin to liberate. Understandably, there is a competition between dislocation loops and VO centers in capturing them. It is not unreasonable to consider that at the initial stage of the emission of Si_Is from the $\mathrm{Si/SiO}_x$ interface, a sizeable percentage of them are trapped by the dislocation loops. At higher temperatures of the annealing procedure, more Si_Is are available for the reaction $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$ to become significant. As a result, the decay of the VO signal is manifested in the spectra at about $\sim 281\,^\circ\mathrm{C}$ [Fig. 2(b)]. In other words, the T_{ann} of the VO center is higher in the samples subjected to thermal treatment under high pressure, in comparison with that of the samples treated under atmospheric pressure, at the same temperature. Both of the above annealing temperatures are lower than that in the untreated sample.

In the sample pretreated at (960 °C, 12 kbar, 5 h) the TEM technique detects even larger oxide precipitates with more extended dislocation loops surrounding them [Fig. 1(c)]. The penetration area of the dislocations accompanying the precipitates is significantly larger. Besides them, dislocation loops not containing any precipitates were observed. The larger size of the precipitates and the higher complexity of the loops around them, are expected to have a greater impact on the situation and the number of the Si_Is at the interface. In other words, since the morphology of the precipitates has not been changed, the number of the Si_Is at the $\mathrm{Si/SiO}_x$ interface and their degree of binding to it is expected to alter. In addition, the capacity of the dislocation loops which are now larger, in capturing the emitted Si_Is, is expected to be bigger. As a consequence, the competing reaction $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$ becomes profound at a higher temperature, i.e., at 291 °C [Fig. 2(c)], where the decay of the VO signal begins to appear in the spectra. On the other hand, the reaction $\mathrm{VO}+\mathrm{O}_i \rightarrow \mathrm{VO}_2$ occurs at $\sim 300\,^\circ\mathrm{C}$, indicating the corresponding appearance of the VO_2 signal in the spectra.

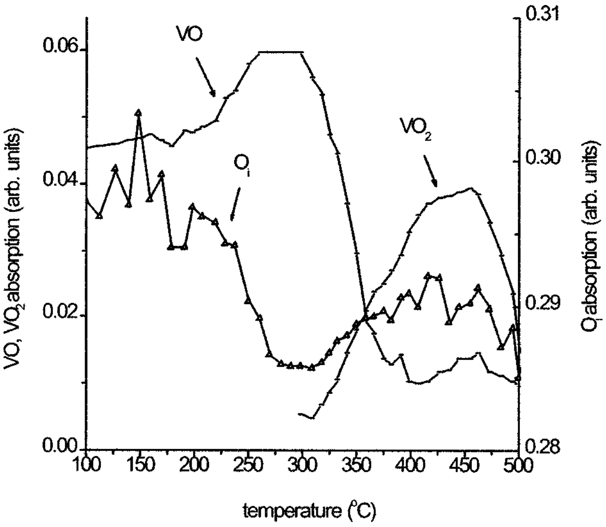

FIG. 3. 15 min isochronal annealing curves of the VO, the VO_2, and the O_i defects in the untreated sample.

In the untreated sample, the decay of the $828\,\mathrm{cm}^{-1}$ band of the VO defect occurs at $\sim 300\,^\circ\mathrm{C}$ (Fig. 3) accompanied, as expected, by the emergence of the $890\,\mathrm{cm}^{-1}$ signal of the VO_2 defect formed according to the reaction $\mathrm{VO}+\mathrm{O}_i \rightarrow \mathrm{VO}_2$. The observed concomitant increase of the $1106\,\mathrm{cm}^{-1}$ signal of the oxygen band strongly indicates that the reaction $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$ also occurs in parallel. We conclude therefore that alternative sources of Si_Is exist. Such sources are large defect clusters present in neutron-irradiated Si. The disordered regions also have Si_Is bound at their periphery and upon dissociation at these temperatures[14] could liberate them. Thus, there are two stages in the emission of the Si_Is: one occurring at temperatures below 300 °C, where Si_Is are emitted from the $\mathrm{Si/SiO}_x$ interface and another occurring from 300 °C onwards, where Si_Is are emitted from large defect clusters. Both stages occur in the pretreated samples while only the latter stage occurs in the untreated sample.

The HT pretreatment causes a large shift of the T_{ann} of the VO center towards lower temperatures (from ~ 300 to 271 °C). The shift of the T_{ann} is smaller with the application of HP (12 kbar), under the same temperature of 870 °C (from 300 to 281 °C), and even smaller with the increase of the temperature of the heat treatment (960 °C) under the same pressure (from 300 to 291 °C). It does not take a lot to figure out the potential here. Under the proper HTHP treatments we can control the evolution curve of the VO defect and most in particular its annealing temperature. Of course, these observations refer to the temperature regime were the morphology of the precipitates is practically the same, that is platelets in our case.

It is important to note that an inverse annealing stage occurring prior to the T_{ann} in the evolution curve of both the untreated and the HT treated sample does not seem to appear in the HTHP treated samples. This stage is the result[15] of the trapping of some additional vacancies, available in the bulk, by O_i atoms, which leads to the formation of the VO centers.

Sources of these vacancies are large defect clusters,[16] dissociated divacancies, and also disordered regions.[17] We argue that in the case of HTHP treated samples, on increasing the temperature during the isothermal annealing sequence, the liberated vacancies are absorbed by the oxygen precipitates and also to some extent by the dislocation loops. Therefore, any additional formation of VO defects is inhibited. However, in the case of HT treated samples, where the precipitates are of smaller magnitude and the strain fields around them are weaker, some of the vacancies are absorbed by the precipitates and some by the O_i atoms to form VO centers. The inverse annealing stage is more profound in the untreated sample because the majority of the available vacancies are trapped by O_i to form VO defects.

CONCLUSIONS

The results of the present study have shown that the application of HT and HTHP pretreatments in Cz-Si samples can affect the evolution curve of the VO defect in Si. In particular the T_{ann} of the VO defect starting around 300 °C for the untreated sample (due to the reaction $\mathrm{VO}+\mathrm{O}_i \rightarrow \mathrm{VO}_2$) is shifted to 271 °C in the HT treated sample at 870 °C. The application of HP of 12 kbar during the heat treatment at this temperature increases the T_{ann} to 281 °C. Further on, the increase of the temperature of the heat treatment from 870 to 960 °C under the 12 kbar pressure causes another increase of the T_{ann} of the VO center to $\sim 291\,°\mathrm{C}$. We have ascribed the phenomenon to the formation of precipitates and other structural defects due to the HT and/or HTHP pretreatments and consequently to the activation of a second reaction that is, the $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$, occurring as a result of the liberation of the Si_Is from the $\mathrm{Si}/\mathrm{SiO}_x$ interface. The degree of binding of the Si_Is at the interface and their available number depends on the HT or/and the HTHP pretreatments and this determines the temperature where the reaction $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$ becomes significant. In essence, it determines the temperature where the VO defects begin to anneal out, since the reaction $\mathrm{VO}+\mathrm{Si}_I \rightarrow \mathrm{O}_i$ precedes the reaction $\mathrm{VO}+\mathrm{O}_i \rightarrow \mathrm{VO}_2$. The absence of a reverse annealing stage in the evolution curve of the VO defect in the HTHP treated samples was attributed to the presence of precipitates and other structural defects, which absorb any liberated vacancies from large defect clusters.

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