Infrared studies of defects formed during postirradiation anneals of Czochralski silicon

C. A. Londos,[a] N. V. Sarlis, and L. G. Fytros
Department of Physics, University of Athens, Solid State Section, Panepistimiopolis, Zografos, Athens 157 84, Greece

(Received 20 April 1998; accepted for publication 25 June 1998)

This article reports on defect studies of neutron-irradiated Czochralski-grown silicon (Cz-Si) material by means of infrared spectroscopy. In particular, the investigation was focused on the evolution of the 828 cm^{-1} well-known band of *A*-center, due to isochronal anneals from room temperature (RT) up to $\approx$700 °C. The strength of the VO band begins to increase above $\approx$200 gradually up to 300 °C (stage I); then, it begins to decrease up to $\approx$400 °C (stage II), where upon it stabilizes up to $\approx$550 °C (stage III). Upon re-irradiation under exactly the same conditions and repeating the annealing process, the increase of the VO signal in stage I disappears. The phenomenon is ascribed to the existence of defect aggregates labeled as X_i centers which are correlated with (impurity-defect) clusters that compete with O_i in capturing vacancies. The presence of X_i centers is related to the thermal annealings performed. Comparison of the evolution of VO (828 cm^{-1}) and VO_2 (887 cm^{-1}) bands between irradiated and re-irradiated materials, during stage II, is made and the results are discussed in the framework of established reaction patterns. The stabilization of the amplitude of the 828 cm^{-1} line in stage III is examined. The prevailing aspect is that a portion of *A*-centers in neutron-irradiated Si acquires larger thermal stability by relaxing in the vicinity of larger defects. © *1998 American Institute of Physics.* [S0021-8979(98)01119-0]

I. INTRODUCTION

A-centers are among the dominant defects created in Czochralski (Cz)-grown Si, submitted to any kind of irradiation at room temperature. The main reason is that monovacancies produced by irradiation are too mobile to survive at such a temperature, and besides annihilation by Si_i or/and pairing with each other to form V_2 defects, they are trapped by O_i, being in large concentration in Cz-Si, to form VO pairs.

The structure and the properties of *A*-center have been extensively investigated by various experimental techniques such as electron paramagnetic resonance (EPR), deep level transient spectroscopy (DLTS), infrared spectroscopy (IR) etc. It is now well-established that an energy level at E_c-0.17 eV and a localized vibrational mode (LVM) band at 828 cm^{-1} are associated with VO. Upon annealing above $\approx$300 °C VO defects become mobile leading to the decay of 828 cm^{-1} line and the parallel growth of 887 cm^{-1} line generally attributed[1] to the VO_2 defect. However, the whole picture about *A*-center is still incomplete. Its evolution with temperature, for example, is not fully understood despite many years of sustained effort.[2]

In this experiment, fast neutrons have been used to produce VO defects in silicon. Upon heat treatment, more complex defects of V_nO_m structure are created. Signals from these defects could be generally traced by IR spectroscopy which has been proved to be a powerful technique for studying vacancy-oxygen complexes in silicon. The main aim of this work is to monitor the annealing behavior of VO defect in an attempt to elucidate the cause of some characteristics in the evolution curve of this defect during isochronal anneals up to 700 °C. More specifically, we try (i) to understand an inverse annealing stage in the temperature range 200–300 °C, (ii) to compare the evolution of VO and VO_2 defects between irradiated and re-irradiated materials, in the temperature range of 300–400 °C, in the framework of the valid aspects for the reaction processes that take place; and finally, (iii) to explain the stabilization of the *A*-center signal in the temperature range 400–500 °C.

II. EXPERIMENT

Cz-grown Si samples, with initial oxygen concentration of $[O_i]_0 \approx 10^{18}$ cm^{-3} were irradiated by fast neutrons at a dose of $\approx 1\times10^{17}n$ cm^{-2} in a water-cooled pool-type reactor. The water temperature did not exceed 50 °C during irradiation. The effect of thermal neutrons was avoided by putting the samples inside Cd foils. 15 min isochronal thermal anneals were performed in open furnaces with the samples inside high-purity quartz tubes. The optical measurements of the vibrational frequencies were taken by a JASCO-IR 700 two beams dispersive spectrometer. Background two-phonon absorption was subtracted during the measurements by using floating-zone (Fz) Si samples of approximately equal thickness with those of Cz-grown samples.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Upon irradiation a percentage of oxygen interstitial atoms is lost from the solution participating in the formation of various defects. If $\Delta[O_i]$ expresses the difference between the initial oxygen concentration $[O_i]_0$ prior to irradiation and

[a]Electronic mail: hlontos@atlas.uoa.gr

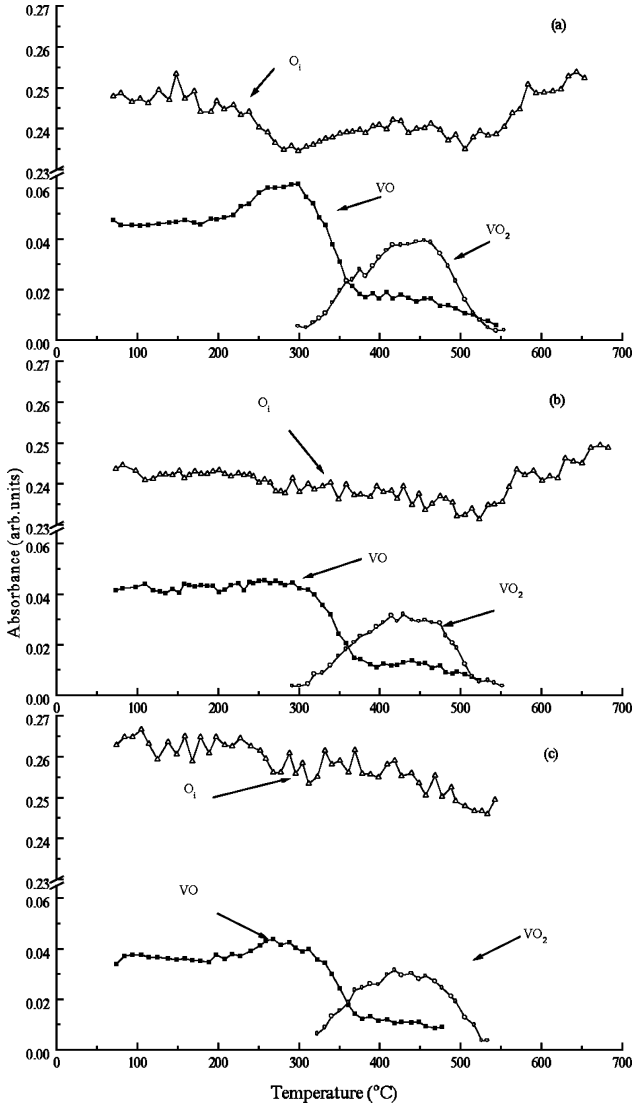

FIG. 1. Annealing behavior of VO, VO_2 and O_i defects: (a) 15 min isochronal annealing sequence after neutron irradiation, (b) the same annealing sequence after the end of the annealing process of (a) and re-irradiation, (c) second re-irradiation and 15 min isochronal annealing sequence of the sample, after the annealing process of (b), and heat treatment at 900 °C for 30 min.

the oxygen concentration after the irradiation then the percentage $\Delta[O_i]/[O_i]_0$ of oxygen loss in our experiments was found to be $\approx 4\%$. Parallel to this, the measurements show that oxygen is gone with an efficiency of $[A]/\Delta[O_i]_0 \approx 84\%$ to the *A*-center. Thus, a small, although not insignificant, percentage of oxygen atoms is lost during irradiation to unknown sinks, presumably forming IR inactive defects or/and other undetected centers. Among the latter, for example, is the V_2O defect expected to form upon irradiation, though in low concentration.

As the annealing temperature increases, the *A*-center band in neutron-irradiated material is distorted by the emergence of satellite bands.[3,4] In this work, the effect of these bands on the *A*-center band was removed[4] by computer deconvolution using Lorentzian profiles.

Figure 1(a) shows the evolution of the 828 cm^{-1} line. The amplitude of the VO center remains constant with annealing temperature up to ≈ 200 °C when it begins to increase, reaching a maximum at ≈ 280 °C, and this persists up to 300 °C (stage I), where it begins to decrease rapidly up to ≈ 400 °C (stage II). In this temperature range the decay of the 828 cm^{-1} band is accompanied by the emergence in the spectra of another band at 887 cm^{-1} generally attributed[1] to a VO_2 defect. Above 400 °C, the amplitude of the *A*-center does not die quickly (as expected) with increasing temperature. A small portion of the peak persists to about 550 °C (stage III). The evolution of the O_i amplitude in the whole annealing temperature range is also shown in Fig. 1.

The evolution of the *A*-center in the temperature range from room temperature up to 700 °C has rarely been a primary concern of investigation. There certainly are points which need to be elucidated in order that the whole picture becomes clearer. In what follows, every temperature stage mentioned above will be examined and discussed separately.

A. Stage I

The increase of the VO signal at this stage certainly indicates an additional production of VO pairs. An interesting feature of neutron damage in silicon is that, besides point defects, large clusters are also produced.[5] Upon increasing the annealing temperature, vacancies liberated[6] from these clusters are trapped by oxygen atoms to form VO pairs. Another source[7] of vacancies may be divacancies which are partially dissociated at these temperatures. The latter process,[8] possibly accounts for the appearance of stage I in electron-irradiated silicon were large clusters of defects are not expected to form.

After completion of the 15 min isochronal annealing sequence up to 700 °C, where all the signals from the various V_nO_m defects in IR spectra have disappeared, in agreement with previous reports,[1] the samples were irradiated again under exactly the same conditions and the same annealing routine was carried out. As is seen from Fig. 1(b), stage I is now not present. This means that no additional *A*-centers were formed. Moreover, the oxygen concentration, although showing a tendency to decrease, during stage I [Fig. 1(b)] this change is much smaller in comparison to that observed in [Fig. 1(a)]. Note, however, that the re-irradiated crystal is not expected to be exactly the same as the initial one. Although all IR signals have disappeared at the end of the annealing, it is quite possible that some defects may have gone irreversibly to some invisible configurations. As is well established[5,9] in the literature, large clusters of defects or mixture of point defects with extended defects presumably IR inactive or undetected due to low concentrations, are formed at higher temperatures. Oxygen precipitation processes are also expected to occur at the latter stages of the anneals. All these definitely indicate that the final situation of the crystal at the end of the annealing sequence is not the same as the initial one. Thus, the following explanation could be put forward in relation to the disappearance of stage I.

In all likelihood, some defects are still present at the end of the annealing process. These defects will be called X_i centers henceforth. Index ''i'' is put to denote the fact that it is likely that more than one type of center might be involved.

As is apparent, it is very difficult, from the present data, to make proper inferences for the nature of X_i centers, since no signal from them has been detected in our spectra. Their presence is indirectly concluded from the experimental findings. Nonetheless, we can make some deductions about their structure from the role attributed to them by analyzing the experimental data. We believe that the absence of stage I is related to the presence of defect clusters. The presence of large aggregates of defects has been previously suggested[5] in the literature. In particular, in our case, X_i centers could be related[10] to impurity-defect clusters[9] appearing in the bulk of the materials. Such defects are expected to anneal out[11] at $T \geqslant 900$ °C. They are surrounded by fields of elastic stresses and have the tendency to capture intrinsic defects. Note that Si material always contains oxygen and carbon, as unintentionally added impurities during processing, and that the heterogeneous association of Si self-interstitials with carbon and oxygen has been proposed[9] to lead to the formation of B defects. In this line of thought, energy levels reported[12] from DLTS studies that appear upon anneals in electron-irradiated Cz-grown Si may have some relevance with regard to the defects we study here. We also note that DLTS and transmission electron microscopy (TEM) studies in high dose ion-implanted Cz-grown silicon have also detected[13] electrical signatures related to defect clusters and extended interstitial defects that evolve from point defects during thermal anneals.

After re-irradiation, on repeating the annealing routine, as the temperature increases, the X_i centers become effective again and at ≈ 200 °C they compete with oxygen in capturing the liberated vacancies. If X_i centers are related with (impurity-defect) clusters, then they are expected[11] to be destroyed upon thermal treatments at higher temperatures. To test this argument, the following experiment was carried out.

After completion of the second isochronal annealing sequence up to ≈ 700 °C, the samples were submitted[10] to an anneal at 900 °C for 30 min. Subsequently, the samples were re-irradiated and then subjected to the usual isochronal annealing process. Stage I is now present [Fig. 1(c)], although the increase of VO is significantly smaller than that of Fig. 1(a). The concentration of O_i in this temperature range also decreases in a similar manner as that of Fig. 1(a). This reappearance of stage I, implicitly suggesting the destruction of X_i centers (at least partially), corroborates our hypothesis. Note that the amplitude of the 828 cm^{-1} line immediately after re-irradiation [Fig. 1(b)] is slightly smaller than the corresponding amplitude after the first irradiation [Fig. 1(a)], a fact consistent with the existence of X_i centers which compete with oxygen in trapping the vacancies. Vacancies could also be trapped by disordered regions. The influence of these regions is expected to become more profound as a result of the increased lattice damage due to the repeated irradiations with neutrons. However, disordered regions are known[14] to anneal out completely at temperatures as high as 600–700 °C and therefore we can exclude, in principle, any relation of them with X_i centers.

Further experiments were also performed in order to check whether pre-irradiation heat treatments affect the evolution of the observed IR bands. To this end, another sample cut from the same wafer, and having similar $[O_i]_0$ was subjected to a heat treatment at 650 °C for 5 h prior to any irradiation. After neutron bombardment and the usual isochronal annealing sequence the evolution curve of VO (Fig. 2) shows a much smaller increase of [VO] during stage I in comparison with that of Fig. 1(a). The latter may indicate either that the performed heat treatment prior to irradiation was not adequate to account for the disappearance of the whole increase of VO during stage I, or that two contributors are involved[8] in the [VO] increase, one of which survived the particular treatment. The main conclusion of the above two experimental processes, i.e., (i) irradiation and then anneal, (ii) anneal and then irradiation, is that thermal treatment in general, is an important factor for the formation of X_i centers or at least for the manifestation of their ability to capture vacancies.

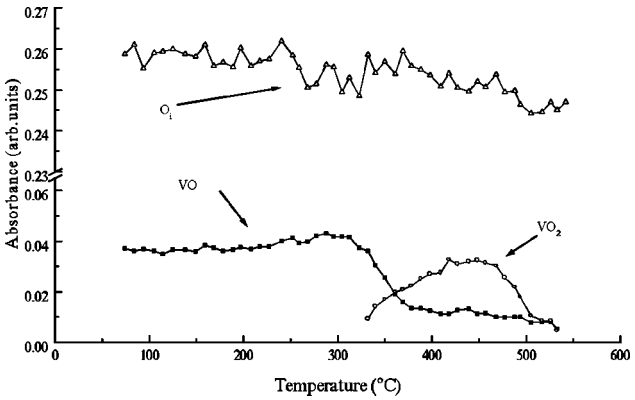

FIG. 2. Annealing behavior of VO, VO_2 and O_i defects for a sample subjected to a prior heat treatment at 650 °C for 5 h and then irradiated.

Apparently, a definite conclusion about the exact identity of X_i centers cannot be reached. A combination of optical and electrical measurements on irradiated and/or unirradiated samples with various oxygen and carbon contents submitted to various anneals at high temperatures is certainly required in order to see whether X_i centers are due to interaction of oxygen with oxygen clusters and/or carbon, or to radiation defects not annealed in neutron irradiated materials above 700 °C.

B. Stage II

1. Post-irradiation anneal

The annealing of the *A*-center and the growth of the VO_2 defect are most likely the result of more than one reaction process occurring simultaneously, as for example: $VO+O_i \rightarrow VO_2$, $VO+VO \rightarrow V_2O_2 \rightarrow VO_2+V$, $VO+Si_i \rightarrow O_i$. In the case of neutron-irradiated material, however, large clusters of defects are formed. These clusters are potential sources of Si_i in the temperature range where the VO signal anneals out. Thus, the destruction of VO by Si_i ($VO+Si_i \rightarrow O_i$) is expected to dominate, a fact that is experimentally indicated by the simultaneous increase of $[O_i]$ [Fig. 1(a)]. In a previous paper,[15] in order to investigate the type of kinetics, we considered three separate scenaria for the destruction of VO and the growth of the VO_2 defect. In all the scenaria the reaction $VO+Si_i \rightarrow O_i$ was considered as the dominant one for the

TABLE I. The decay of VO and the growth of VO_2 in the re-irradiated sample.

Scenario	Activation energies	Correlation coefficient
(I)		
$VO+O_i \rightarrow VO_2$	$E_1=(1.23\pm0.35)$ eV	$r_1=0.870$
(II)		
$VO+VO \rightarrow VO_2+V$	$E_2=(1.80\pm0.40)$ eV	$r_2=0.937$

decay of VO. Actually, the data fit with second-order kinetics in agreement with the fact that the reaction $VO+Si_i \rightarrow O_i$ could be approximately considered[15] as a second-order one. In the first scenario, the growth of VO_2 was studied by first-order kinetics corresponding to the reaction $VO+O_i \rightarrow VO_2$. In the second scenario, the formation of VO_2 was studied by second-order kinetics, tentatively corresponding to a reaction process where two VO come together by a diffusion process and then a vacancy is liberated $(VO+VO \rightarrow VO_2+V)$. Finally, in the third scenario both the reactions $VO+O_i \rightarrow VO_2$ and $VO+VO \rightarrow VO_2+V$ were considered as taking place simultaneously and mixed kinetics was used to analyze and study the data. Activation energies derived from the various scenaria are listed in Table I of Ref. 15.

2. Post-reirradiation anneal

In the case of re-irradiated material our data for the decay of VO again fit with second order kinetics. However, we notice immediately [Fig. 1(b)] the absence of a concomitant increase of $[O_i]$ during the decay of VO. This is an indication that the destruction of VO by Si_i does not occur in this case. This behavior is most likely related to the presence of X_i centers now in the material, which apparently act as sinks for the Si_i's. The growth of VO_2 could be correlated either with the first-order reaction $VO+O_i \rightarrow VO_2$ [scenario (I)] or with the second order reaction $VO+VO \rightarrow V_2O_2 \rightarrow VO_2+V$ [scenario (II)]. The results are summarized in Table I. An activation energy of $E_1=1.23$ eV [scenario (I)] is apparently not reasonable for the formation of VO_2. Also, the corresponding correlation coefficient is small. In scenario (II), the concomitant changes of VO and VO_2 concentrations could be described by the reaction $VO+VO \rightarrow VO_2+V$. An activation energy $E_2=1.80$ eV is calculated. The curve fitting to this reaction has a higher correlation coefficient and therefore describes better the experimental data. We can not help remarking however to the reaction $VO+O_i \rightarrow VO_2$ is expected to be preferable to the reaction $VO+VO \rightarrow VO_2+V$, since $[O_i] \gg [VO]$ for the VO decay. Nevertheless, our data fit better with a second order reaction. Note that in the first reaction the moving agents VO meet with the immobile O_i atoms, although in the second reaction VO defects meet each other. On a physical basis, and purely qualitatively, these remarks support the interpretation of our findings, on the grounds that the diffusion coefficient of VO is much higher[2] than that of O_i, and also that the capture radius for the reaction between VO's is expected to be larger than that between VO and O_i.

Mixed kinetics [scenario (III)] where the decay of VO is described by the reaction $VO+VO \rightarrow VO_2+V$ and the growth of VO_2 by the reactions $VO+VO \rightarrow VO_2+V$, $VO+O_i \rightarrow VO_2$ does not lead to a reliable determination of the activation energies from our data since the corresponding values of the correlation coefficients were always smaller than 0.70. Therefore this scenario was not included in Table I.

C. Stage III

As is seen from Figs. 1(a) and 1(b), above 400 °C the strength of the VO pair becomes more or less stable. A small portion of the signal remains in the spectra up to ≈550 °C. Notice that even at higher temperatures, traces of the *A*-center signal might be detected but they are barely discernable above the noise level and therefore the corresponding experimental points are not depicted in the figures. The phenomenon appears[1] also in electron irradiated material. Two possibilities exist:

(i) At a certain stage of the annealing sequence, processes leading to reformation of *A*-centers occur. The whole behavior of VO-center evolution, in the temperature range 400–550 °C, appears to reflect a dynamic process where an almost steady state situation is achieved when the rate of loss of *A*-centers equals the rate of their regrowth. The stabilization of the *A*-center amplitude, at first sight, gives the impression of a balance between opposing processes which lead to the destruction and generation of VO defect at equal rates. In other words, the thermally-induced annealing of *A*-centers is compensated by the formation of new defects. As an extension to the above explanation the following aspect could be considered. Irradiation-induced vacancies accumulated in the material are gradually released from defect clusters on increasing the temperature. These vacancies trapped by O_i tend to replenish the *A*-centers lost, consequently delaying their anneal out.

(ii) VO centers in silicon are normally isolated defects. However, a small fraction of *A*-centers possibly stabilize[10] in the vicinity of other larger defects. This may increase their thermal stability. The higher thermal stability is related to an increase of the binding energy of these centers due to additional elastic stresses in their environment. Apparently, it is more difficult for these defects to anneal out and therefore their signal remains in the spectra up to higher temperatures, thus broadening their annealing range. Noticeably, analysis of data from defect studies in neutron-irradiated Si has shown a tendency of vacancy-oxygen complexes to form preferably near disordered regions[16] and having in principle a higher annealing temperature. It is worth noting at this point, that a similar behavior, where a LVM signal from a defect stabilizes with temperature after a rapid decay, has also been reported in proton and deuteron implanted InP.[17]

Notice that previous reported DLTS work[18,19] shows that the E_c-0.17 eV peak of the *A*-center anneals out at temperatures ranging from 300–400 °C without further stabilization of the DLTS signal. Furthermore, its disappearance is not accompanied by the emergence of another peak in the DLTS spectra. These results of electrical measurements are not inconsistent with the second possibility mentioned above. It is possible that the modified *A*-centers are electrically inactive and therefore they are undetected by the DLTS technique.

On the other hand, if their vibrational unit is slightly affected in its structure, the corresponding LVM signal is expected to be very close to that of the usual *A*-center. It is this signal that remains in the IR spectra at higher temperatures due to the larger thermal stability of the modified defects. In other words, the absence of a DLTS signal to accompany the decay of the E_c-0.17 eV peak of *A*-center when the latter dies out, in comparison with the emergence of the 887 cm^{-1} IR band when 828 cm^{-1} band of *A*-center dies out is not something unexpected if one associates the 887 cm^{-1} IR band with the VO_2 defect which is electrically inactive[2] and therefore cannot be traced by DLTS.

Another feature in the spectra should also be mentioned: interestingly, the final amplitude of the oxygen peak has attained values higher than the initial one. This is a characteristic trait of oxygen behavior in Si previously reported in the literature.[20] Oxygen in silicon is located dominantly at interstitial sites. However, it is also present[21] in a variety of agglomerate configurations. During annealing, these oxygen atoms are released and participate in various reaction processes that take place. In the short run, during the annealing sequence the influence of these additional oxygen atoms is not particularly obvious in the spectra. However, in the long run, at high annealing temperatures where all defects disappear and oxygen atoms return to the most favorable interstitial configuration, these additional atoms initially released from agglomerates could make up for the difference between the final and the initial oxygen concentrations.

IV. CONCLUSIONS

In conclusion, the evolution of the *A*-center 828 cm^{-1} IR band created in neutron-irradiated material has been monitored by isochronal annealing studies up to $\approx$700 °C. An inverse annealing stage in the temperature range 200–300 °C has been attributed to the availability of additional vacancies liberated from defect clusters. These vacancies are readily captured by isolated oxygen interstitial atoms to form additional *A*-centers. Upon re-irradiation when repeating the annealing sequence the inverse annealing stage disappeared. Its absence was tentatively attributed to the existence of defect clusters, the X_i centers, which compete with oxygen in capturing vacancies. Our experiments indicate that their presence is related to the heat treatments performed. The exact nature of X_i centers is an open question, although certain defect structures, i.e., (impurity-defect) centers previously reported in the literature could be considered as potential candidates. The evolution of VO and VO_2 defects was studied and comparison was made in their behavior between the irradiated and the re-irradiated material. Within the framework of previously established reaction patterns activation energies for the VO decay and the VO_2 growth were provided for the re-irradiated samples. The stabilization of VO signal above 400 °C was discussed and some explanations were put forward. It seems that a number of *A*-centers relax in the vicinity of larger defects, a fact that leads to an increase of the binding energy of VO pairs and therefore to an increase of their thermal stability.

[1] J. Corbett, G. Watkins, and R. McDonald, Phys. Rev. **135**, A1381 (1964).
[2] B. Svenson and J. Lindström, Phys. Rev. B **34**, 8709 (1986).
[3] A. Ramdas and M. Rao, Phys. Rev. **142**, 451 (1966).
[4] N. Sarlis, C. Londos, and L. Fytros, J. Appl. Phys. **81**, 1645 (1997).
[5] R. Newman and R. Jones, in *Semiconductors and Semimetals*, edited by F. Shimura (Academic, New York, 1994), Vol. 42, p. 289.
[6] H. Stein, in *2nd International Conference on Neutron Transmutation Doping in Semiconductors*, edited by J. M. Meese (Plenum, New York, 1979).
[7] L. Berman, V. Voronkov, V. Korlov, and A. Remenguk, Sov. Phys. Semicond. **26**, 847 (1992).
[8] M. Trauwaert, J. Vanhellemont, A. Van Bavel, P. Clauws, A. Stesmans, H. Maes, and G. Langouche, in *Oxygen '96. Early stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer, Dordrecht, 1996), Vol. 17, p. 501.
[9] K. Ravi, *Imperfections and Impurities in Semiconductor Silicon* (Wiley, New York, 1981).
[10] V. Emtsev (private communication).
[11] P. Lugakov and V. Luk'yanitsa, Sov. Phys. Semicond. **26**, 848 (1992).
[12] A. Awadelkarim, W. Weman, B. Svenson, and J. Lindström, J. Appl. Phys. **60**, 1974 (1986).
[13] J. Benton, S. Libertino, P. Kringhoj, D. Eaglesham, J. Poate, and S. Coffa, J. Appl. Phys. **82**, 120 (1997).
[14] L. Khirenenko, Y. Pomozov, V. Shekhovtsov, V. Shinkerenko, and V. Yashnik, Defect Diffus. Forum **103–105**, 293 (1993).
[15] C. Londos, N. Sarlis, and L. Fytros, Phys. Status Solidi A **163**, 325 (1997).
[16] V. Akhmetov, V. Bolotov, L. Lmirov, and V. Khavchenko, Phys. Status Solidi A **75**, 601 (1983).
[17] D. Fischer, M. Manasreh, D. Talwar, and G. Matous, J. Appl. Phys. **73**, 78 (1993).
[18] L. Kimerling, in *International Conference on Radiation Effects in Semiconductors, Dubrovnic 1976 Inst. Phys. Conf. Ser. No 31*, edited by N. Urli and J. Corbett (IOP Publishing, Bristol, 1977), p. 221.
[19] C. Londos, Phys. Status Solidi A **113**, 503 (1989).
[20] J. Lindström, G. Oerhein, and J. Corbett, Phys. Status Solidi A **95**, 179 (1986).
[21] W. Kaiser, H. Frisch, and H. Reiss, Phys. Rev. **112**, 1546 (1958).