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Strategies to suppress A-center formation in silicon and germanium from a mass action analysis viewpoint

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Experimental and theoretical techniques are used to investigate the impact of tin doping on the formation and the thermal stability of the A-center in electron-irradiated Czochralski silicon and its conversion to the VO_2 defects. Previous experimental studies are consistent with the viewpoint that tin (and other oversized isovalent atoms) doping suppresses the formation of the A- center. The results are discussed in view of recent density functional theory calculations, whereas we employ mass action analysis to calculate the impact of isovalent dopants on the suppression of the A-center. We propose point defect engineering strategies to contain the concentration of the deleterious A-centers in silicon and in related materials such as germanium.
Keywords: A-centers, point defects, electron-irradiations, doping.

Представлены результаты экспериментальных и теоретических исследований влияния допирования оловом на формирование и термостабильность А-центров в облученных электронами кристаллах кремния, полученных методом Чохральского, а также процессов их преобразования в дефекты вида VO_2. Экспериментальные исследования подтверждают, что допирование оловом (равно как и другие неизовалентные замещения) подавляет образование А-центров. Полученные результаты обсуждаются с учетом последних теоретических расчетов функциональной плотности. Высказано предположение о том, что точечные дефекты способствуют понижению концентрации А-центров в кремнии и сопутствующих материалах, таких как германий.
Ключевые слова: А-центры, точечные дефекты, облучение электронами, допирование.

Представлені результати експериментальних і теоретичних досліджень впливу допування оловом на формування та термостабільність А-центрів в опромінених електронами кристалах кремнію, отриманих методом Чохральського, а також процесів їх перетворення в дефекти виду VO_2. Експериментальні дослідження підтверджують, що допування оловом (так само як і інші неізовалентні заміщення) пригнічує утворення А-центрів. Отримані результати обговорюються з урахуванням останніх теоретичних розрахунків функціональної густини. Висловлено припущення про те, що точкові дефекти сприяють зниженню концентрації А-центрів у кремнії і супутніх матеріалах, таких як германій.
Ключові слова: А-центри, точкові дефекти, опромінення електронами, допування.

Silicon (Si) is the dominant material for a range of applications (including microelectronic devices, detectors, photovoltaics and nuclear medicine), whereas germanium (Ge) is gaining ground in the past few years for applications in nanoelectronics due to its advantageous material properties.[1-10] Irrespective of decades of research the detailed understanding of numerous defect-dopant interactions, which can affect its properties are not well established.[11-13] for both materials defect-dopant interactions are becoming increasingly important as the characteristic dimension of devices are a few nanometers and hence atomic effects play a more significant role.

Oxygen (O) in Si and Ge is introduced during crystal growth by the Czochralski method. In both materials, oxygen intersitials (O_i) can trap lattice vacancies to form vacancy-oxygen pairs (known as *V*O or A-centers). When the temperature is increased A-centers form larger oxygen-vacancy defects (VO_2).[14, 15] In Si, A-centers are both electrically [16, 17] and optically active,[18] whereas VO_2 clusters are only optically active. [18] It is therefore important to suppress the formation of A-centers via point defect engineering strategies. In that respect the early experimental studies of Watkins [19] and Kimerling *et al.* [20] determined that isovalent impurities [carbon (C), germanium (Ge) and tin (Sn)] can modify the formation processes of A-centers in Si.

Sn is introduced in Si or Ge at ever increasing concentrations leading to the variation of the lattice parameter and electronic properties (i.e. band gap) in Sn-doped Si or Ge.[21-23] At high Sn-concentrations the resulting alloys (i.e. GeSn, SiSn, and SiGeSn) exhibit interesting properties which can deviate to what is

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expected by SiGe alloys.[21,23-26] Interestingly, in early electron irradiation experiments Sn was introduced in Si to suppress the formation of the A-center.[27] In recent studies, employing infrared spectroscopy in conjunction with density functional theory calculations the impact of Sn doping in Si was investigated at an atomic scale level.[10,28,29]

In the present study we discuss recent results on the impact of Sn doping on the formation of the *V*O defect and its conversion to VO_2 defect in electron-irradiated Si. We extend these findings by employing mass action analysis to discuss possible point defect engineering strategies to suppress the concentration of A-centers and other defect clusters in Si and Ge.

Figures 1(a) and 1(b) demonstrate the evolution with temperature of the *V*O and VO_2 bands for the Sn-poor ([Sn] = 3×10^{17} cm^{-3}) and Sn-rich ([Sn] = 9×10^{18} cm^{-3}) electron-irradiated Si samples, respectively (details of the experimental methodology, the samples and the results are given in Ref. 30). From Fig 1(b) it can be observed that the production of the A-center is suppressed in the Sn-rich sample. This is consistent with previous experimental evidence [refer to Fig. 1(b)].[31-33] Importantly, the vacancies that mainly formed during the irradiation and which did not recombine with self-interstitials, can associate with Sn atoms to form Sn*V* pairs. Notably previous work calculated that the full-*V* (Sn substitutional next to a *V*) and the split-*V* configuration (Sn surrounded by two semi-vacancies) are comparable in energy with the later being more stable by only 0.02 eV (Ref. 23 and references therein). When Sn is introduced in Si it will compete with oxygen to capture vacancies. This in turn will result in the suppression of the *V*O concentration. In Si, the Sn*V* pair will dissociate via the reaction Sn*V* → Sn + *V* at a low temperature (near 170 °C). The Sn*V* pair is infrared inactive, however, its presence and its annihilation in Si can be established by the changes of the concentration of other defects such as the *V*O pair. [31-33] The dissociation of

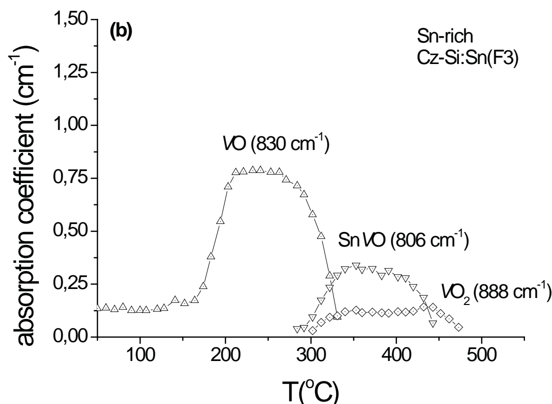

Fig. 1. The thermal evolution of the *V*O, the VO_2 and the Sn*V*O defects for the (a) Sn-poor and (b) Sn-rich samples.

Sn*V* pairs at 170 °C is accompanied by the steep increase in the concentration of the absorption coefficient of *V*O [refer to Fig. 1(b)]. This increase in the *V*O content at 170 °C is not observed in the Sn-poor case indicating that the formation of SnV pairs and subsequently the impact of Sn doping on the A-center is negligible if the Sn content of the sample is low (the impact of Sn content is discussed further through mass-action analysis below). Importantly, the final *V*O concentration of the *V*O defect in the Sn-rich sample is smaller than that in the Sn-poor sample. Another important result is that the conversion of the *V*O to the VO_2 defect is suppressed in the Sn-rich sample (Fig. 1). This is attributed to the trapping of migrating *V*O pairs by Sn to form Sn*V*O clusters, in agreement with previous investigations.[34] Further experimental investigations are necessary to gain a detailed understanding of the impact of Sn doping on the formation and thermal evolution of the A-center as well as its conversion to the VO_2 defect.

The experimental results provide information on the thermal stability and formation of the defect clusters. In this sense they can be linked to the DFT results, which provide evidence of the binding energies, E_b, defined by:

$$E_b = E_{defect\ cluster} - \Sigma E_{isolated\ defects}.$$

According to this definition, negative binding energies imply that a cluster is energetically favorable with respect to its constituent isolated components.

Considering the DFT-derived binding energies of the Sn*V* (-1.30 eV) [35] and the *V*O pairs (-1.32 eV) [36] they are different by only 0.02 eV. Given their similar stability what will be important in order to assess which pair will have the highest concentration is the relative concentration of tin, [Sn], and oxygen, [O]. These can be linked to the concentrations of the Sn*V* pair, [Sn*V*], and *V*O pairs, [*V*O] *via* mass action analysis[37]

$$\frac{[SnV]}{[Sn][V]} = \exp\left[\frac{-E_b(SnV)}{k_B T}\right] \tag{1}$$

$$\frac{[VO]}{[O][V]} = \exp\left[\frac{-E_b(VO)}{k_B T}\right] \tag{2}$$

Where [*V*] is the concentration of the *V*, k_B is Boltzmann's constant and T is the temperature. As the binding energies of Sn*V* and *V*O are approximately equal:

$$\frac{[SnV]}{[VO]} = \frac{[Sn]}{[O]} \tag{3}$$

This simple relation indicates that the capture efficiency of *V* by Sn and O is directly related to the initial concentrations of [Sn] and [O]. Therefore, in Sn-poor sample it is expected that the [*V*O] concentration will be more than 3 times higher than [Sn*V*], whereas for the Sn-rich sample the relative concentration of [Sn*V*] will be an

order of magnitude higher than [VO]. Considering Fig. 1 we estimate an Sn concentration of 2.4 x 10^{16} cm^{-3} for the Sn-poor sample and 1 x 10^{17} cm^{-3} for the Sn-rich sample.

Considering the mass action analysis arguments discussed above there are two strategies that can be implemented: (A) dope with Sn at concentrations that exceed the concentration of oxygen in the lattice and (B) dope with other isovalent dopants, which attract vacancies with binding energies higher than that of the A-center. Can these point defect engineering strategies be applied to other related materials and issues?

Moving our focus to alternative substrates such as Ge similar arguments can be used. In Ge, the SnV pair is bound by -0.64 eV,[38] whereas the VO by -0.45 eV.[39] Therefore, in Ge the SnV is more stable compared to VO by about -0.2 eV in contrast to Si where the two pairs were almost equally bound. Considering again mass action analysis arguments in the case of Ge:

$$\frac{[SnV]}{[VO]}=\frac{[Sn]}{[O]}\exp\left[\frac{-E_b(SnV)+E_b(VO)}{k_BT}\right]= =\frac{[Sn]}{[O]}\exp\left(\frac{0.19eV}{k_BT}\right) \quad (4).$$

Therefore there is an enhancement of the trapping of Sn by the temperature dependent factor exp(0.19eV/k_BT). This is an important difference in the behavior of Sn-doped Si and Ge. For example, if we consider that [Sn] = [O] = 10^{18} cm^{-3} at 443 K (i.e. the point where SnV in Si dissociates) the ratio [SnV]/[VO] will be 1 for Si but 145 for Ge. Therefore, the trapping of V by Sn in Ge is at least two orders of magnitude higher than in Si.

This treatment assumes that there are no other competing V-related clusters at the temperature range where the VO and SnV pairs exist and that the [V] is constant between the two samples. Also mass action analysis corresponds to the equilibrium behaviour of defects towards which the system tries to evolve. Finally, the kinetics can play a role hindering the system to reach the equilibrium state.

Table I.

Calculated binding energies (eV) for the capture of V by O_i or oversized isovalent dopants in Si and Ge.

Defect reaction	Si	Ge
$V + O_i \rightarrow VO$	-1.32[a]	-0.45[d]
V + Ge → GeV	-0.27[b]	-
V + Sn → SnV	-1.30[b]	-0.64[e]
V + Zr → ZrV	-	-1.89[f]
V + Hf → HfV	-	-1.85[f]

[a]-[36]; [b]-[35]; [c]-[..]; [d]-[39]; [e]-[38]; [f]-[44]

Interestingly the recent study of Markevich *et al.*[40] correlated the association of Sn-V in phosphorous (P) doped Ge with the suppression of the transient enhanced diffusion of P. The suppression of the vacancy-mediated diffusion of *n*-type dopants such as P in Ge is a matter of active research and a range of codoping strategies have been proposed.[41-43] The introduction of an isovalent dopant in Ge with a high binding energy with respect to V would readily form pairs with vacancies that will have increased thermal stability. In a recent DFT work [44] (using the same methodology as in [36, 38, 43]) it is calculated that the binding energies of the zirconium-V (ZrV) and hafnium-V (HfV) pairs in Ge are -1.89 eV and -1.85 eV respectively. Therefore, we propose that doping with Hf or Zr can prove an efficient strategy to trap vacancies in clusters thus constraining their participation in defect processes such as the formation of A-centers or the enhanced diffusion of *n*-type dopants.

In essence A-centers and oxygen-related clusters in Ge can be effectively completely annihilated by the addition of Sn of equal content to oxygen. Considering oxygen interstitials in Ge have a significantly lower concentration than in Si and that Sn can be dissolved in the Ge lattice for concentrations up to at least 10% (i.e. far higher than the O existing in Ge) this point defects engineering strategy will be effective. The present approach does not consider the kinetics of the processes and how the inclusion of Sn might impact other dopants existing in the device. For example, in *n*-type doped regions phosphorous will also be present at high concentrations. In recent density functional theory studies by Tahini *et al.*[45,46] it was calculated that Sn traps vacancies and that codoping P with large isovalent dopants such as Sn or Hf will lead to the retardation of P. This in turn is important as P is a fast diffusing dopant in Ge hindering the formation of well defined regions that are crucial for devices. The inclusion of Sn or Hf will result in the suppression of the VO concentration and the phosphorous diffusion.

The experimental results determine that the production of VO defect is largely suppressed in Sn-doped Si due to the capture of vacancies by the Sn atoms. This in turn leads to the reduction of the conversion of VO to VO_2 due to the formation of SnVO clusters. Using mass action analysis it is calculated that the key is to capture the lattice vacancies. There are two point defect strategies that can be implemented to control the concentration of A-center: (A) dope with Sn at concentrations that exceed the concentration of oxygen in the lattice and (B) dope with other isovalent dopants, which attract vacancies with binding energies higher than that of the A-center. In Ge it is calculated that the Sn trapping of vacancies will be enhanced by a temperature dependent factor. Finally, we propose that doping Ge with Zr or Hf is an efficient way to

trap vacancies and suppress the *V*O formation. The present work illustrates how DFT calculations can initiate actions for the point defect engineering of materials.

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