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Impact of the size 4 cluster on low temperature indium diffusion in silicon

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Abstract

Using *ab initio* density functional theory the configuration space of indium clusters in silicon up to size 4 is explored. The strongest binding energy corresponds to a cluster containing one indium and three self-interstitials. Two plausible configurations almost degenerate in energy are found: the ⟨100⟩ I_4 model and an alternative which combines two ⟨110⟩ split di-interstitials. The segregation of indium to a InI_4 cluster is found to capture the dual peak and the low temperature annealing behaviour of indium.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Supersteep retrograde (SSR) profiles are required to serve the needs of channel engineering of sub-100 nm metal–oxide–semiconductor field effect transistors (MOSFETs) [1, 2]. An SSR profile has its peak located in the bulk of the silicon as indicated by the dashed curve in figure 1(a). Such a profile shows a gentle variation of threshold voltage with decreasing channel length, leading to a significant improvement in process tolerance. This is illustrated in the target threshold voltage values depicted within the square in figure 1(b) corresponding to the two profiles of figure 1(a). The SSR profile can also be engineered to achieve superior transistor characteristics (higher on-to-off state current ratio) as illustrated in figure 1(c).

There has been considerable interest in recent years in exploring indium as a potential candidate for obtaining SSR profiles in N-MOS devices [3–5]. In comparison to boron, indium has a heavier mass and a higher coefficient of segregation into the oxide which results in a natural retrograde profile at the interface as indicated in figure 1(d) [6]. This segregation coefficient, which is the ratio of the concentration of dopant in the silicon to that in silicon dioxide, has been calculated as $m(T) = \frac{C_{Si}}{C_{oxide}} = m_0 \exp(-E_m/kT)$, with pre-exponential factor $m_0 = 1.3 \times 10^{-13}$ and activation energy $E_m = -2.55$ eV [7]. Here k is the Boltzmann

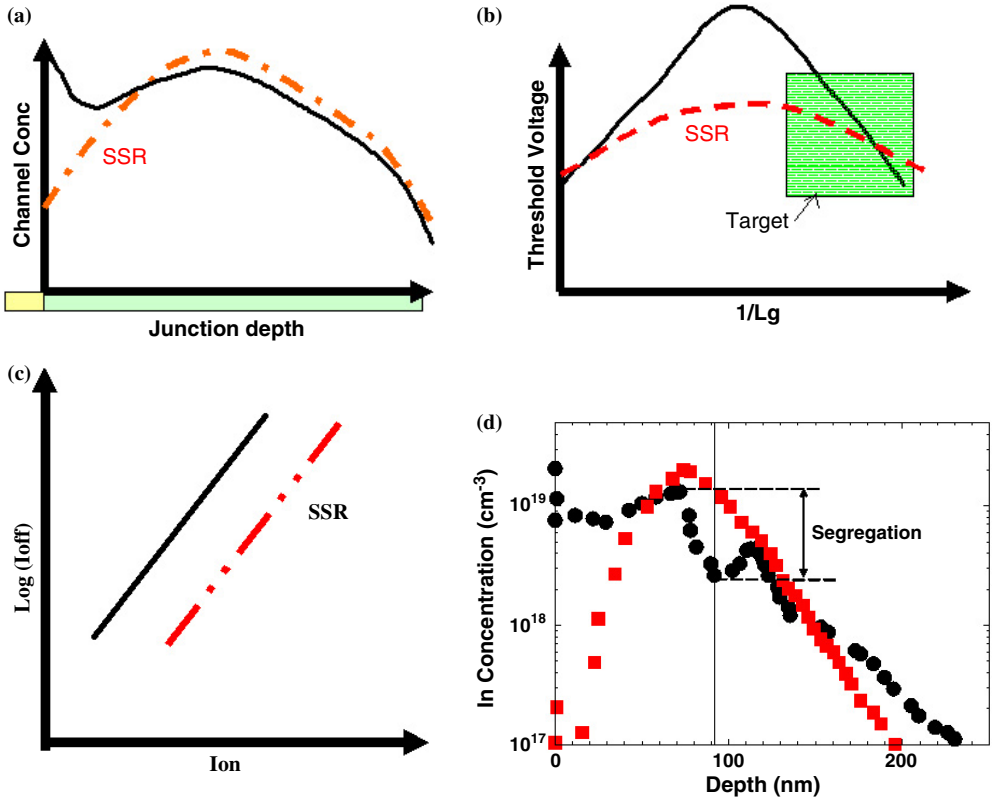

Figure 1. (a) Illustration of an ideal supersteep retrograde (SSR) channel profile (dashed line) in comparison to a profile with dopant pile-up (solid line) for sub-100 nm technologies. (b) Illustration of threshold voltage versus reciprocal gate length for the dopant profiles of figure 1(a). (c) Illustration of ratio of on to off state currents for the dopant profiles in figure 1(a). (d) Illustration of segregation of indium into oxide. Data taken from [6].

constant and T the temperature. In comparison, the segregation coefficient of boron is given by $m(T) = 9.82\exp(-0.29\,eV/kT)$ [8].

The diffusion of indium into silicon was first proposed to be due to mixed interstitialcy and vacancy mechanisms [9]. Griffin *et al* observed a significant enhancement of indium in the presence of interstitials generated by implantation damage. The fractional contribution due to the interstitialcy mechanism of 80% was found, similar to that of boron [10]. The diffusion coefficient D was calculated by Suzuki as being primarily due to neutral species and given by $D = 1.443\exp(-3.5645\,eV/kT)$ [11]. Noda demonstrated that under high dose implantation conditions, indium generates a buried amorphous layer resulting in a dual-peak profile [12]. His Monte Carlo simulations revealed the failure of the '+1' model, due to the heavier mass of indium. Additionally Noda reported a strong segregation of indium to the end-of-range (EOR) dislocation loops and a defect kinetics dominated by interactions of indium atoms with self-interstitial clusters. Further studies by Solmi [13] revealed that the faster dissolution of indium atoms in the peak closer to the surface could not be explained by the standard diffusion of indium atoms de-trapped from dislocation loops. An enhanced diffusivity of indium at the peak closer to the interface was required to explain the data. Furthermore, the dose loss of indium during high temperature annealing could not be explained by segregation alone but

required the incorporation of small interstitial clusters and {311} defects [14]. The motivation of this work is therefore to develop a physical model for indium segregation to EOR loops based on an understanding of the stability of small interstitial clusters.

The methodology explored herein is via detailed first-principles calculations within the framework of density functional theory. The stability of small interstitial clusters containing various ratios of indium to self-interstitials in silicon is evaluated. The strongest binding is found to be that for a self-interstitial rich cluster of size 4 (InI_4). Using continuum modelling, the dual-peak profile of indium is found to be satisfactorily modelled for low temperature annealing, using the stability of this cluster.

2. Methodology

Calculations were carried out using density functional theory implemented in VASP [15, 16]. For the exchange correlation the local density approximation [17] was used. The interaction between ions and valence electrons was described using ultrasoft Vanderbilt pseudopotentials [18] and the wavefunctions were expanded in plane waves with a cut-off energy of 150 eV. The binding energies were found to be invariant with cut-offs up to 300 eV. For integration of the Brillouin zone four special k-points generated by the Monkhorst–Pack method [19] were used. The supercell consisted of 64 atoms of crystalline silicon plus additional indium atoms. The relaxation of all configurations presented was carried out until the forces did not exceed 0.005 eV $Å^{-1}$. The configuration space was explored by trying out new methods of cluster evolution and comparing their formation energy with respect to those of well-known self-interstitial clusters reported in the literature. Charge state effects were taken into account for the mid-gap position of the Fermi level. The binding energies of the most favourable clusters were then calculated with reference to a previous cluster, with the released product being either the InI (indium interstitial) or the self-interstitial (I) and maintaining charge neutrality at all times. Hence the binding energy is given by

$$E_{\text{binding}}(\text{In}_n\text{I}_m) = [E(\text{In}_n\text{I}_m) + E_{\text{bulk}}(\text{Si}_{64})] - [E(\text{In}_n\text{I}_{m-1}) + E(\text{I})] \tag{1}$$

or

$$E_{\text{binding}}(\text{In}_n\text{I}_m) = [E(\text{In}_n\text{I}_m) + E_{\text{bulk}}(\text{Si}_{64})] - [E(\text{In}_{n-1}\text{I}_{m-1}) + E(\text{In}_{\text{int}})]. \tag{2}$$

3. Results

3.1. Theory

Calculations reveal that the most stable sites of interstitial indium are the bond centred (bc) and ⟨100⟩ split interstitials (figures 2(a) and (b) respectively), where the configuration sites refer to atoms *prior* to relaxation. This is explicitly stated because the symmetry of final relaxed sites is different from that in the initial positions. In these sites, the indium atom is pushed to the substitutional lattice site after relaxation, whereas the silicon atom is displaced into the interstitial site.

The aggregation of indium via substitutional sites is found energetically unfavourable in comparison to the interstitial sites. Methods of cluster growth of indium atoms are explored using capture through either favourable indium interstitials or the ground state ⟨110⟩ self-interstitial. The ratio of indium to self-interstitials in each of these clusters (In_nI_m) is varied, where n refers to the number of indium atoms and m the number of self-interstitials in the cluster. In the initial stages indium prefers a self-interstitial rich cluster growth process in comparison to that which is indium rich. For example for two indium atoms, in a cluster

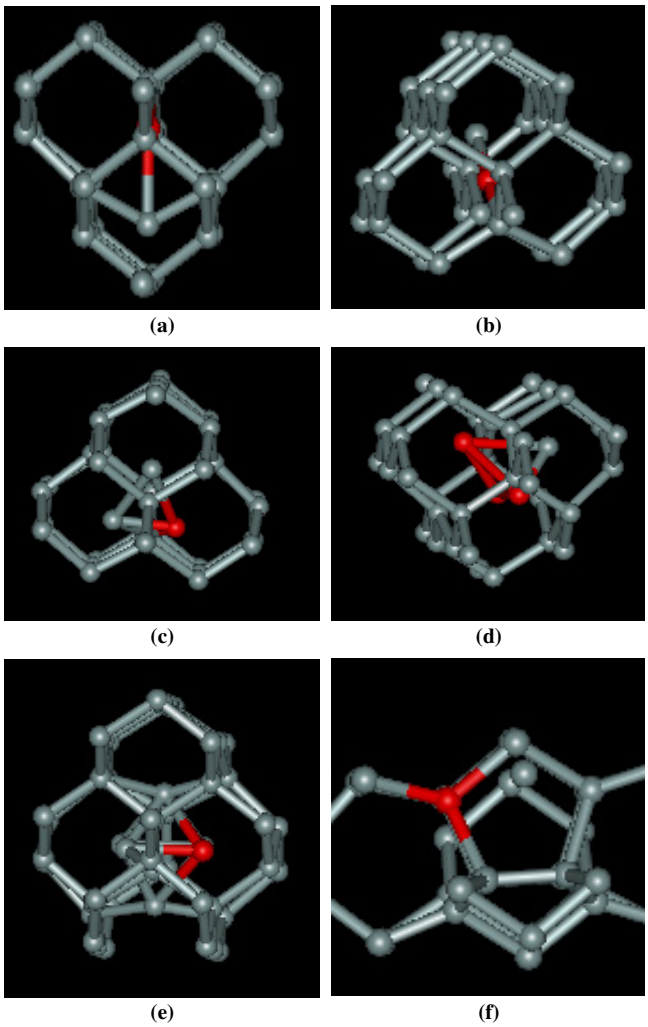

Figure 2. (a) Split ⟨100⟩ and (b) bond centred configurations of indium interstitial in silicon. (c) Di-interstitial cluster with one indium atom (InI_2). (d) Tri-interstitial cluster with one indium atom (InI_3). (e) Four-interstitial model consisting of two di-interstitial clusters. (f) Four-interstitial model proposed by Arai *et al* [23].

(In_2I) the total energy difference with InI_2 is −7.465 eV. Moreover, when the ratio of indium atoms in the clusters are increased beyond 1, configurations based on the split ⟨110⟩ are more favourable than other structures.

When considering growth via the ⟨110⟩ self-interstitial path, clusters proposed earlier in [20] are considered. This growth mechanism for precursors has been demonstrated to proceed up to the stage where capture of chain-like defects required for the formation of {311} clusters becomes favourable. For the case of two interstitial atoms, the C_{1h} di-interstitial formed by the capture of the ⟨110⟩ split interstitial is considered [21]. In the C_{1h} model, three atoms (two interstitials and one lattice atom) share a single lattice site (figure 2(c)). The tri-interstitial model consists of four atoms (three interstitials and one lattice atom) sharing a single lattice site in the shape of a perfect tetrahedron (figure 2(d)) [22].

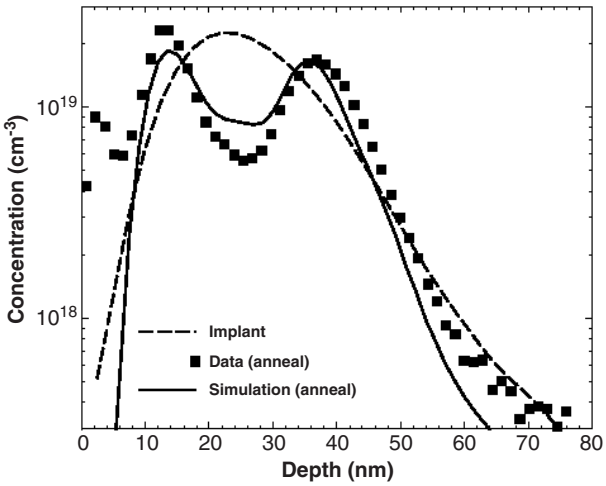

Figure 3. A comparison of experiment with the model based on In–I_4 cluster capture at 585 °C, 45 min annealing.

For the case of the four-interstitial model two alternatives exist: the lowest energy structure is the I_4 structure proposed by Arai *et al* (figure 2(f)) which requires the aggregation of four ⟨100⟩ interstitials [23]. Alternately, the low energy structure formed by the combination of two di-interstitials of C_{1h} symmetry, consists of six atoms that form a prism with two triangular bases (figure 2(e)) [20]. This route for the formation of the four-interstitial model can be considered plausible because of the mobility of the di-interstitial as reported by Estreicher *et al* [24]. For self-interstitials alone, the Arai model in the 64-atom supercell results in a formation energy of 1.8 eV per interstitial whereas the cluster with two di-interstitials has a formation energy of 2.06 eV per interstitial. With one indium atom replacing one of the self-interstitials in the Arai model, the binding energy of 3.27 eV is obtained, which is the highest in comparison to all other clusters of size 4 or less. The alternative four-interstitial model is almost degenerate in energy with only 0.1 eV difference between the two structures. The enhanced stability of the size 4 cluster is not surprising, since it has been proposed that stability of size 4 and size 8 self-interstitial clusters is critical for reproducing self-interstitial supersaturation during early stages of TED, prior to the formation of {311} clusters [25].

3.2. Experiment

Amorphizing indium doses are implanted and regrown at temperatures that result in solid phase epitaxy (SPE). Figure 3 indicates the SIMS results after a 585 °C/45 min anneal. Ninety per cent of the implanted dose lies within the silicon after anneal. This suggests minimal dose loss associated with the regrowth of the amorphous layer.

The as-implanted damage profile is simulated using the Monte Carlo implant (TRIM). A buried amorphous layer (200–400 Å) is used in the simulations. The continuum model is based upon three discrete rate equations for compact self-interstitial clusters up to size 4 and a two-moment model for {311} defects. The model has been well calibrated [26] with experimental data on interstitial supersaturation obtained previously in [25]. The capture of indium by these small self-interstitial clusters is implemented in this work. Figure 3 indicates the indium distribution at low temperatures after a 45 min anneal. The stability of the InI_4 model is found to model the dual-peak profile behaviour of indium diffusion in silicon.

4. Conclusion

Two alternative models for a size 4 InI_4 cluster, almost degenerate in energy, are found to be most stable among all clusters incorporating indium up to size 4. One structure is based on the I_4 model proposed by Arai [23], whereas the second structure is a combination of two C_{1h} di-interstitials [21]. The stability of this structure is demonstrated to reproduce the dual-peak profile behaviour of indium diffusion in silicon at 585 °C via continuum simulations.

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