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Dissolution kinetics of B clusters in crystalline Si

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Abstract

Boron (B) clustering in crystalline Si induced by interaction with Si self-interstitials is a widely studied phenomenon of fundamental importance for Si micro- and nano-electronic technology. The requested B activation increase brings the B concentration to a very high level and a detailed understanding of B clustering at high concentration is demanded. In the present work we present some recent results regarding the B clustering process starting from B concentration both below and above the B solubility limit. We show that B clusters, produced by self-interstitial interaction with substitutional B in crystalline Si, dissolve under annealing according to two distinct paths with very different characteristic times. The two regimes generally coexist, but while the faster dissolution path is predominant for clusters formed at low B concentration (1×10^{19} B/cm^3), the slower one is characteristic of clusters formed above the solubility limit and dominates the dissolution process at high B concentration (2×10^{20} B/cm^3). The activation energies of both processes are characterized and discussed. It is shown that the faster path can be connected to a direct emission of mobile B from small clusters, while the slower path is demonstrated not to be self-interstitial limited and it is probably related to a more complex cluster dissolution process.

Keywords: Dissolution; B clustering; Crystalline Si

1. Introduction

Boron (B) clustering is a widely studied phenomenon due to its detrimental effect on the dopant activation in Si and it is therefore a relevant topic for micro- and nano-electronics technology. At equilibrium, B incorporates into crystalline Si in substitutional sites up to a solid solubility concentration, which depends on the temperature [1]. Above this solid solubility limit (s.l.) B precipitates and, under the effect of very high thermal budgets, it reaches equilibrium with a conjugate crystalline boride phase containing both B and Si [1].

Generally, boron is introduced in the lattice by ion implantation. In this case, B clusterizes even at concentration below its solubility limit due to the interaction with the point defects excess induced by ion implantation [2–10]. The presence of such clusters is generally deduced by the presence of an immobile (not diffusive) and electrically inactive portion of the B concentration profile. Moreover, these clusters formed below the solubility limit are very small and not directly detectable by structural techniques such as transmission electron microscopy (TEM). The clusters are formed both by B and by self-interstitial defects (I) produced by the ion implantation process. In fact, it is largely demonstrated that B clustering reduces both the self-interstitial clusters formation and the amount of I, which promotes the transient enhanced diffusion (TED) of B [7,9–12].

Moreover, many small clusters containing both B and Is are theoretically demonstrated to be energetically favoured [13–16]. Even if only up to 4 B atoms and 4 I defects are generally considered in these calculations, tens of possible boron interstitial clusters (BICs) are predicted. Such clusters transform one into the other in the formation (dissolution) process by two possible paths that are the capture (release) of an I or a BI mobile species. A full description of the formation and dissolution of the BICs must take into account the energy barrier for each release and capture process together with the proper boundary conditions that describe the evolution of I supersaturation during the annealing of the ion implantation damage. Different kinds of models, describing the cluster evolution, are proposed in literature [4,17,18] based on ab-initio calculated barriers [17], inverse modeling over experimental data [4] and simplified models considering only a subset of the calculated BIC [18]. In this scenario different sets of values for the cluster energy barriers are reported and differences also of 1 eV are also present comparing different tabulations. Even a more complicated situation is present when

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the case of both B and I supersaturation is considered. This experimental situation is typical when high B doses are implanted in Si at low energy in order to obtain extremely high-doped shallow junction, as demanded by technological progress.

Relatively few works have investigated this latter regime in detail. In some papers the clustering that occurs at high B concentration is explained in terms of the same BIC model based on inverse modeling energetics used to describe low concentration clustering [19,20]. Other authors report the presence of an anomalous B diffusion (boron enhanced diffusion, BED) that dominates over the transient enhanced diffusion effect at very high B concentration (above 2×10^{21} at/cm^3) [21]. They explain this phenomenon by the formation of a boride phase that gives a large volume expansion to the Si lattice and induces the injection of a further amount of Si self-interstitials besides those induced by ion implantation. Other authors again report by TEM analysis the presence of large clusters containing B. Such clusters are not a separate phase and dissolve by an Oswald ripening process [22]. Therefore, the knowledge of the B cluster formation and dissolution is still far from a coherent picture, especially close or above the B s.l., which is a regime particularly interesting for technological applications.

One important topic regarding boron clusters is the experimental study of the dissolution (reactivation) process that clusters undergo under prolonged thermal annealing. This aspect is relevant since it gives information about the dynamics of B reactivation and, moreover, it can be used as a test for the models that describe the evolution of boron clusters. Recently, we measured activation energy of 3.2 ± 0.4 eV [10] for cluster dissolution formed at low B concentration (below the s.l.) under controlled interaction between substitutional B and Si ion implantation damage. This is in agreement with electrical reactivation energy barrier obtained under direct B ion implantation [23]. On the other hand, higher dissolution barriers [24] or longer dissolution times [3] are reported in some literature data. In particular, refs. [24,5,6] explain the highest dissolution energy with the need of BICs to get external interstitials (slowly provided under equilibrium conditions) to dissolve, while in ref. [10] an I supersaturation is reported to accompany the B dissolution, indicating the emission of both B and I by the clusters. As far as the high B concentration case is concerned, recently, electrical reactivation of B after high-dose low energy ion implantation was investigated by Mokhberi et al. [19] and an energy barrier to the B electrical reactivation of 4.7 eV was determined.

In this paper we report a systematic investigation of the dissolution mechanisms of B clusters formed by Si ion implantation on samples containing substitutional B in a wide range of concentration, either above or below the s.l. The kinetics of the B and I emission from the clusters are investigated in detail.

The underlying idea is to investigate the B and I release from the clusters after the end of the I supersaturation induced by the implantation damage. In this case the boundary conditions of the system are strongly simplified since only the clustered B is out of equilibrium in the samples. The goal is to get a direct insight on the key steps that are responsible for the clusters' dissolution and, therefore, obtain information on the main cluster families involved in the process. We show that two dissolution paths are present with very different characteristic times, energy barriers and prefactors. The faster path is present both above and below the solubility limit while the slower path is only present at high B concentration. The faster path is accompanied by a slightly I supersaturation (I emission from the BICs) while no supersaturation is detected on the slower path. Further data are presented, obtained by repeating the B dissolution process under the influence of a slight externally induced supersaturation (dry oxidation). These experiments demonstrate that neither the faster nor the slower paths are interstitial limited dissolution processes. We interpreted the presented phenomenology by considering that the faster path is related to the dissolution of usually small clusters, which form both above and below the solubility limit and dissolve by a direct emission of mobile species, while different clusters are formed at higher B concentration. Such clusters undergo a more complex dissolution path and cannot be connected to small B-rich clusters having I-limited reactivation process.

2. Experimental

In the present experiment boron clusters were produced by interaction between interstitial-Si and substitutional B. As done in past experiments [3,4,10], the substitutional B was introduced in Si lattice by epitaxial technique. This allows obtaining very sharp B profiles ensuring an accurate analysis of the B diffusion after the different process steps of the experiment. In particular, three different samples with a common structure were grown by molecular beam epitaxy (MBE), with a 15 nm thick B box placed at a depth of about 230 nm, followed by deeper B deltas. A fourth sample without the box and only with the deltas was grown as a reference. The boxes have concentrations ranging from 1×10^{19} to 2×10^{20} at/cm^3. The deltas have a peak concentration of about 1×10^{18} at/cm^3 and they were used to monitor the B diffusivity and therefore the I supersaturation (see Fig. 1) [3,4,7,25].

After MBE growth, B was fully substitutional, as confirmed by measurements of the strain by high resolution X-ray diffraction [26] and of the substitutional fraction by nuclear reaction

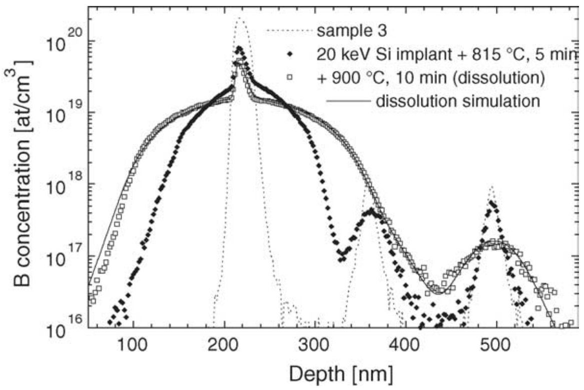

Fig. 1. SIMS boron concentration profile (dashed line) of the sample 3 (B box: 2×10^{20} B/cm^3). Implantation (20 keV, 1×10^{14} Si/cm^2) and thermal annealing (815 °C, 5 min) induce B clustering (diamonds). Further annealing (900 °C, 10 min) induces B clusters dissolution (open squares). Simulation of the dissolution process is also displayed (continuous line).