

Quality of silicon substrate and point defects (4) Precipitate nucleation and vacancy

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シリコン結晶基板の品質と点欠陥(4) 酸素析出の核形成と空孔の関係

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Oxygen precipitation has both detrimental and beneficial effects on silicon device yield and performance. For the “precipitate engineering” [1], the understanding of its nucleation mechanism is continuously progressing as summarized below.

1 Homogeneous nucleation model (Freeland [2]) In 1977, Freeland et al. proposed the homogeneous nucleation model. They observed the increase of precipitates after annealing at 1200 °C by preannealing at 700 °C and assigned it as the nucleation. They determined the supercooling as 80 °C, and thought the critical nucleus included 200 atoms and critical radius was 10 Å.

2 Measurement of nucleation rate and analysis by the classical nucleation theory (Inoue [3, 4], homogeneous nucleation (Osaka [5]), heterogeneous nucleation (Wada[6]) Till 1979, Inoue et al. developed the methods to measure the precipitate volume density and the nucleation rate by utilizing the low-to-high 2 step annealing. We determined the dependence of the nucleation rate on the oxygen content and annealing temperature. We analyzed it by the classical nucleation theory and showed that it follows the phenomenological equation. The fitting parameter, surface energy of precipitate, was obtained to be about 400 erg/cm² and the critical radius at 800 °C is about 4 Å. From that the supercooling required for the nucleation is over 300 °C, homogeneous nucleation model was supported [5]. We showed that Freeland observed the growth of grown-in precipitates above the critical size at 700 °C. We found the large oxide precipitates in the periphery of the crystal where the interface is inclined and attributed them to the heterogeneous nucleation [6].

3 Modified homogeneous nucleation, role of vacancy (Hu [7]) In 1981, Hu proposed the modified homogeneous nucleation mechanism. He pointed out that the swirl like precipitate distribution and precipitation retardation by high temperature preannealing were not explained by the simple homogeneous nucleation mechanism. He suggested that vacancy enhances the precipitation [7]. It is the turnover of his previous result that precipitation emits the self-interstitials (which form the stacking fault). We analyzed the retardation of precipitation by the high temperature preannealing to be due to the induction time [8].

4 OSF ring (Hasebe[9]) and AOP (Harada [10]) observed in V-region After the Voronkov criterion: “the vacancy/interstitial microdefect type is determined by the V/G ratio [11],” was well accepted, relation of precipitation and vacancy took attention. OSF (oxidation induced stacking fault) ring was named by Hasebe [9] because the OSFs were formed in the periphery of the Si wafer. This is the result of our findings that (1) the large oxide precipitates were formed in the periphery [6] as described above and (2) SF was nucleated at the edge of some size of platelet precipitate [12]. Also it was clarified that OSFs are present in the V-rich region [13] where oxide precipitation is enhanced as described next. Anomalous oxygen precipitation (AOP) by the stop of growth and quenching [10] was reported and later it was found to be present in the V-rich region [14] also.

5 Successive nucleation of voids and OP by the supersaturation of O and V (Voronkov [15]) Plekhanov suggested the possibility of homogeneous nucleation by supersaturation of vacancies [16]. We proposed the heterogeneous nucleation at the oxide inner wall [17]. Voronkov [15] proposed that the voids and OP are nucleated successively by the supersaturation of oxygen and vacancy which formed VO₂ at high temperature. IR detection of VO_n is tried [18]. The gettering using rapid thermal annealing (RTA) which quenching in the excess vacancies was developed [19], which is closely related to AOP.

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