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Difficulties in Doping SiGe Alloys with Transition Metal Point Defects

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Introduction Point defects in silicon have been studied extensively for decades [1]. The energy structure of single substitutional impurities and more complex structures has often been determined by high resolution spectroscopy [2] such as photothermal ionisation spetroscopy (PTIS) and absorption measurements. These studies comprised not only defects such as substitutional chalcogens [3] but also transition metals, as for example Au [4] or interstitial iron [5]. Similar results were obtained in germanium which allowed detailed studies at very low impurity concentrations and consequently with very sharp line spectra [6].

In comparison with silicon and germanium, very little is known about the electronic properties of point defects in SiGe alloys. This is particularly true for bulk crystals and includes impurities which are fast diffusers in bulk silicon and germanium. Though SiGe crystals of rather low germanium content have been exposed to a variety of impurities at high temperatures for several days, with one exception [7] no line spectra were observed neither in absorption nor in PTIS. This is in particular true for impurities such as chalcogens and iron.

Comprehensive studies on silicon and germanium have shown that deep donors are obviously more easily incorporated in silicon than in germanium and that germanium probably is more easily doped with deep acceptors than silicon. The question therefore arises [7] whether these properties have anything to do with the absence of line spectra for most impurities in SiGe alloys and whether or not these impurities are actually incorporated. On the other hand, if these impurities are incorporated it was not clear why they would behave so differently in the alloy.

In this note we present a study of SiGe crystalline alloys of various compositions which have been prepared by different techniques and which have been exposed to Au and Cu at elevated temperatures. Evidence is provided that the impurities are actually incorporated but that the impurities precipitate at extended defects and that the concentration of point defects therefore decreases considerably. It will also be shown that, similar to thin layers, the concentration of extended defects increases with increasing germanium content in the crystalline alloys which have been available for this study.

Experimental SiGe monocrystals obtained from a Czochralski (Cz) growth process as well as chemical vapor deposited (CVD) monocrystalline SiGe alloys [8], 1 to 2 mm in thickness, were used for this study. The first ones were available in concentrations up to 9% Ge and the second ones in concentrations up to 50% Ge.

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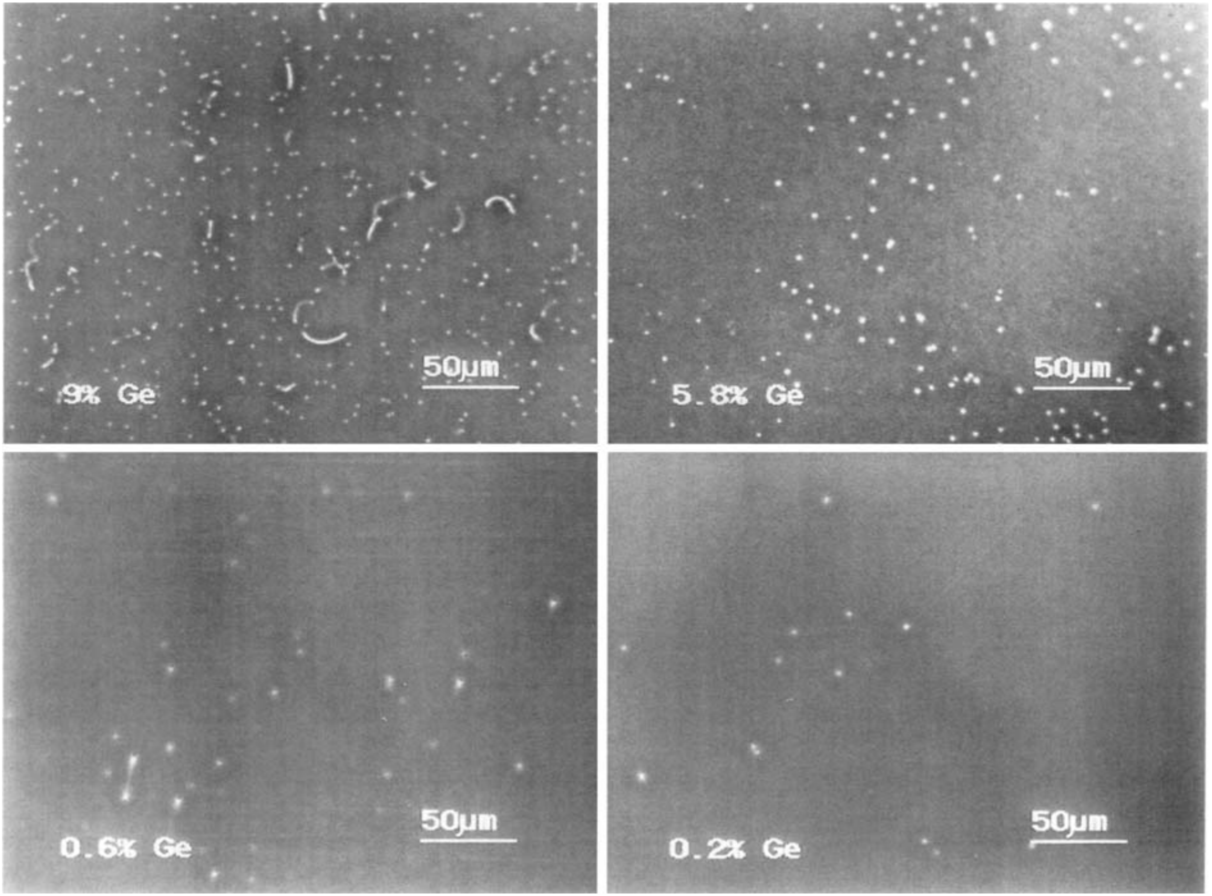

Fig. 1. Etched surfaces of Cz-SiGe samples of different Ge concentrations observed in interference phase contrast

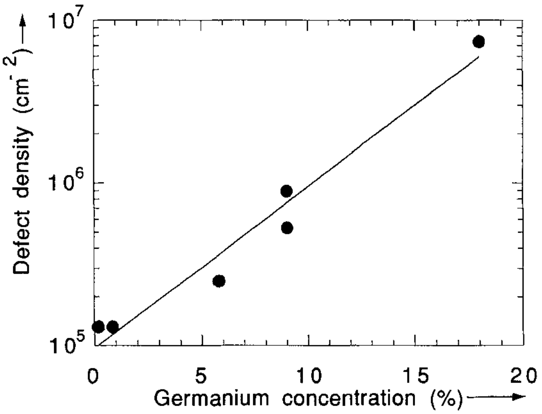

Fig. 2. Defect density of Cz-SiGe and CVD-SiGe alloys vs. Ge concentration

Copper and gold were diffused at temperatures up to 1300 °C for periods up to 4 d in an inert gas atmosphere. Afterwards the samples were quickly quenched in ethylene glycol.

The extended crystal defects of the starting samples were studied using interference phase contrast microscopy. Prior to these investigations the samples were etched with the Yang etchant [9]. The crystalline defects of transition metal doped samples were studied by infrared transmission microscopy as well as by interference phase contrast microscopy.

The total concentration of gold in the doped samples was measured by secondary ion mass spectroscopy (SIMS). In order to minimize the influence of lateral inhomogeneities of the gold distribution a large measurement area of 450×450 μm^2 has been used.

Results Fig. 1 shows the etched surfaces of the Cz-SiGe samples with different Ge concentrations. The crystal defects are primarily dislocations which are visible as white points or lines. Their concentration increased with the Ge concentration of the samples.

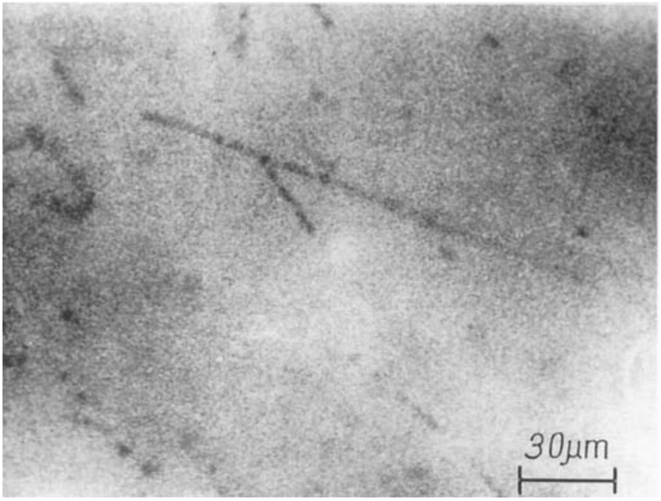

Fig. 3. Infrared transmission micrograph of a Cz-SiGe alloy with 0.6% Ge

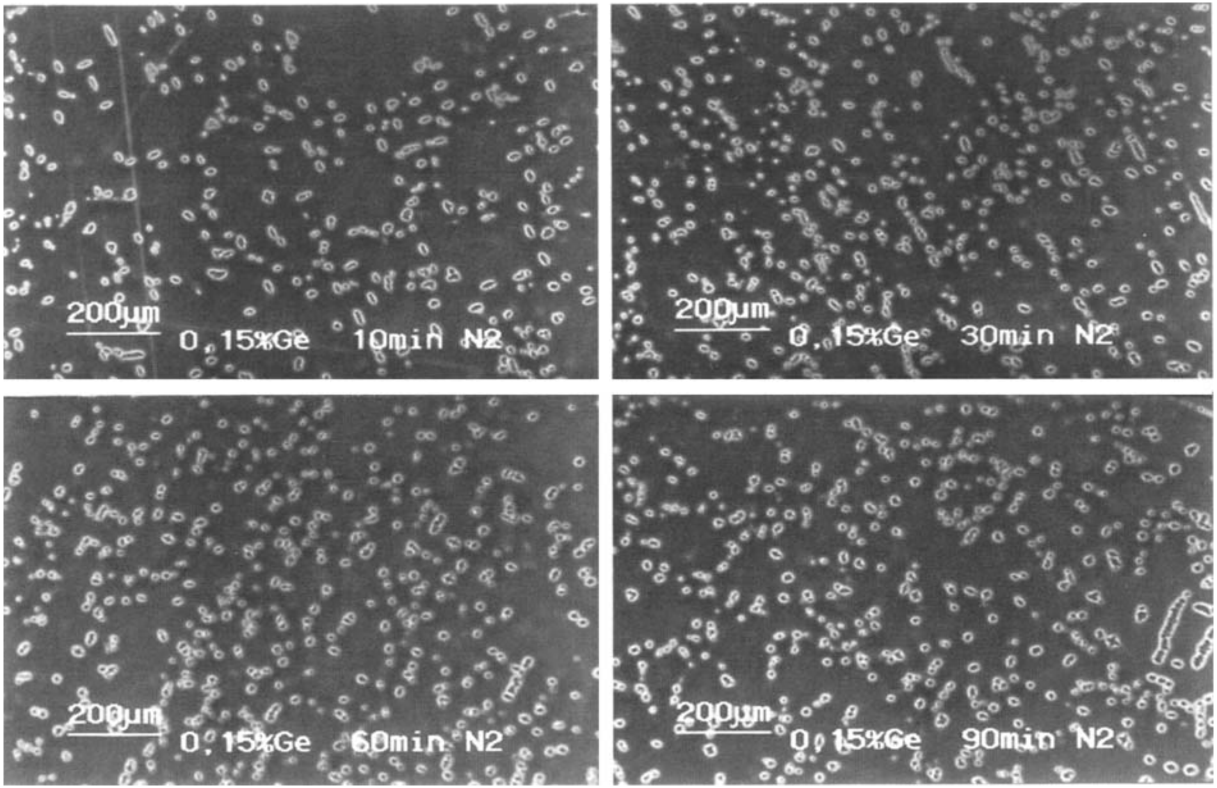

Fig. 4. Etched surfaces of copper doped Cz-SiGe samples with 0.15% Ge after different periods of annealing in nitrogen at 1000 °C as observed in interference phase contrast

Similar results were obtained in CVD-SiGe. The defect density increased exponentially with the Ge concentration for concentrations up to 20% Ge as shown in Fig. 2.

A gold doped Cz-SiGe sample with 0.6% Ge showing no signal in deep level transient spectroscopy (DLTS) and infrared transmission spectroscopy, respectively, was studied in more detail. The total gold concentration of this sample derived from SIMS measurements was 6×10^{16} cm^{-3} indicating that gold indeed was present in the sample. A careful study of the sample by infrared transmission microscopy revealed a high concentration of gold decorated dislocations. Some of them are clearly visible in Fig. 3. Obviously, most of the indiffused gold precipitated at dislocations which drastically reduced the concentration of interstitial and substitutional gold. This effect is well exploited in silicon device processing and often used to getter transition metal impurities from the active device area to extended defects [10]. Additional reasons why line spectra of point defects were not observed in this sample could stem from random potential fluctuations and alloy broadening. Such effects may drastically reduce the amplitudes of the lines and, hence, make it more difficult to resolve them.

Similar results were obtained with copper. One of the Cz-SiGe samples with 0.15% Ge has been doped with copper at 1000 °C in nitrogen for different periods of time. The results are exhibited in Fig. 4. All etch figures which are visible in the figures are caused by dislocations decorated with copper. There is no change in the etch figure arrangement with increasing annealing time. The typical homogeneously nucleated copper silicide precipitate colonies [11] were never observed, which further supports our argument that most of the transition metals were gettered by dislocations.

Conclusions The data presented in this note suggest that the main difficulties in doping SiGe alloys with transition metals, probably, arise from dislocations which getter the indiffused transition metals. The density of dislocations increases exponentially with the Ge concentration in both Cz-SiGe and CVD-SiGe. Since the impurities obviously easily precipitate at dislocations the difficulty of doping SiGe alloys with deep levels increases strongly with the Ge concentration. This is in agreement with previous results obtained by Hellquist et al. [7]. In addition, random potential fluctuations and alloy broadening may contribute to the difficulties in observing well resolved line spectra of point defects in SiGe monocrystalline alloys.

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