An Electron Diffraction and High-Resolution Transmission Electron Microscopy Study of Defect Structure in Silicon Doped with Transition Metal Impurities

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Abstract—Features of defect formation upon the decomposition of a supersaturated solid solution of a transition metal in silicon were studied. Zinc was used as the transition metal impurity. The silicon was doped with zinc by high-temperature diffusion annealing with subsequent quenching. Microstructures of this material were studied by electron diffraction and high-resolution X-ray transmission electron microscopy combined with X-ray energy-dispersion microanalysis. It was established that the studied material was a quite perfect single crystal but contained chaotically distributed dislocations.

DOI: 10.3103/S1062873810070294

INTRODUCTION

Features of microdefect formation at the early stages of the decomposition of a supersaturated solid solution of transition metals in silicon are of interest not only for clarifying the nucleation mechanism, but also for revealing regularities in the subsequent transformation of the defect medium. Transmission electron microscopy (TEM), optical microscopy, and electron beam induced current (IC) in a scanning electron microscope (SEM-EBIC) are most often used to study the formation of microdefects upon the decomposition of a supersaturated solid solution of transition metals in single-crystal Si.

In [1], defects with sizes of several microns were revealed by SEM-EBIC in n-Si(Zn) samples in which zinc was introduced by high-temperature diffusion annealing with subsequent quenching. Their images resemble those of precipitates, as they differed in size and contrast. In the case of precipitates, this was due to the defects being located at different depths. Some of them, however, could have been due to other defects, e.g., dislocations.

The same samples were also studied by X-ray diffuse scattering. Defects of two types with different signs of the power and symmetry of the dislocation fields were found: spherical microdefects of the vacancy type (presumably clusters of point defects) with an average size of around 70 nm and macrodefects of the interstitial type having a flat form (presumably dislocations and narrow-angle boundaries) with sizes of around 2 μm [2]. Despite its high sensitivity, however, the latter is an indirect method and does not provide a complete picture of the nature of defects.

In this work, we used electron diffraction at an accelerating voltage of 75 kV and high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 300 kV in combination with X-ray energy-dispersion microanalysis to study microstructures of such material. Optical microscopy and photoluminescence were used as supplemental methods.

EXPERIMENTAL

Silicon of the n type, preliminarily doped with phosphorus having the concentration \(N_p = 1.5 \times 10^{14} \text{cm}^{-3}\), was studied. The concentration of zinc introduced at a temperature of 900°C over 8 h was \(N_{Zn} = 10^{14} \text{cm}^{-3}\). After diffusion annealing in pumped ampoules, the latter were quenched in water. A U-profile of the distribution of the transition metal concentration with its uncontrolled increase close to the flat boundaries of the plate is usually observed when silicon is doped with transition metal admixtures by diffusion annealing. Around 50–70 μm of silicon (depending on the diffusion time) were therefore ground from each side of the plate after compensation. The plate was then processed in one manner or another, depending on the immediate task.

In silicon compensated by zinc, the upper zinc energy level \(E_n = (E_C - 0.55) \text{eV}\) was partially occupied with the filling function \(f = 0.5\), while the lower level \(E_V = (E_V + 0.31) \text{eV}\) was completely occupied. The concentration of the majority charge carriers (electrons) was \(n = 2 \times 10^{11} \text{cm}^{-3}\), several orders of magni-
tude lower than the concentrations of the introduced admixtures (phosphorus and zinc). The experiment was performed at temperature $T = 300$ K, at which all of the phosphorus was ionized.

For electron diffraction studies, the sample was prepared as follows. Chemical–mechanical polishing was used after polishing with different diamond pastes of gradually decreasing grain size. Finally, the plate was etched in a polishing solution in the ratio HF: HNO$_3$: H$_2$O = 1:1:10 to remove the approximately 1-$\mu$m-thick destroyed surface layer. The size of the samples was 5.0 $\times$ 5.0 $\times$ 0.8 mm$^3$.

For HRTEM studies, the samples were first mechanically thinned to a thickness of about 50 $\mu$m. They were then glued on a copper ring with a diameter of 3 mm and thinned in an ion etching setup.

For optical microscopy studies, the samples were prepared as follows. A standard prepared sample was (as in, e.g., electron diffraction) selectively etched in a Senko mixture of acids K$_2$Cr$_2$O$_7$:HF = 1:1. The samples had the size of 2.4 $\times$ 1.6 $\times$ 0.8 mm$^3$. Samples of this type were also used for photoluminescence and electron diffraction.

RESULTS AND DISCUSSION

Figure 1a shows an electronogram of an $n$-Si(Zn) sample. The interplane distance in the crystal lattice was determined from the relation 
\[ d = \frac{L \lambda}{r} \]
where $L$ is the distance from the dispersion sample to the photographic plate; $\lambda$ is the de Broglie wavelength of an electron, as determined by its energy according to the known relation 
\[ \lambda(\text{Å}) = \frac{12}{E(eV)}^{1/2} \]
and $r$ is the distance from the reflex to the central spot in the electron diffraction pattern created by the non-scattered electrons. It was established that the interplane distance determined for a series of reflexes along the normal to the shadow of the sample surface is $d = 3.14$ that indicates the orientation of the substrate along the [111] plane. Kikuchi lines (light and dark bands) in the electron diffraction pattern [3] reveal the perfection of the $n$-Si(Zn) sample’s single crystalline structure. A bright-field HRTEM image [4] of the studied sample depicting the two-dimensional silicon crystalline lattice is shown in Fig. 1b. It follows that the studied region of the $n$-Si(Zn) sample is a quite perfect single crystal.

Figure 1c shows its Fourier transform. The interplane distance corresponding to the interplane distance for the [111] planes was determined from the distance between the reflexes in it. Figure 1d shows a filtered HRTEM-image of the two-dimensional atomic lattice of the studied sample.

Data from an energy-dispersion microanalysis performed using a probe with a diameter of 2–50 nm at several points of the sample (Fig. 2a) and by scanning along the line are shown in Fig. 2b. No Zn peaks are present in the spectrum, since its concentration in the sample $N_{\text{Zn}} = 10^{14}$ cm$^{-3}$ is less than the sensitivity threshold of the instrument. The copper (Cu) and carbon (C) peaks in the spectrum originate from the technological preparation of the sample for HRTEM.