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Recombination activity of nickel in nitrogen-doped Czochralski silicon treated by rapid thermal processing

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Abstract

The recombination activities of nickel (Ni) in *p*-type nitrogen-doped Czochralski (NCZ) silicon (Si) subjected to the rapid thermal processing (RTP) under different temperatures, atmospheres or cooling rates were investigated by means of microwave photoconductivity decay and scanning infrared microscopy. It was found that the value of the reciprocal of effective minority carrier lifetime ($1/\tau_{eff}$) of NCZ Si, related to the recombination activity of Ni, increased with the annealing temperature or cooling rate, while, it was almost insensitive of the annealing atmosphere. Moreover, the $1/\tau_{eff}$ of the Ni-contaminated NCZ Si was lower than that of the Ni-contaminated conventional Czochralski (CZ) Si annealed under the same condition. It is considered that the nitrogen-related defects or large grown-in oxygen precipitates might be the reason of relative lower recombination activity of Ni in NCZ Si.

Keywords: Czochralski silicon; Nickel; Lifetime; Nitrogen doped

1. Introduction

Nickel (Ni) is one of the most important transition metals, which could contaminate silicon (Si) from stainless-steel equipments and chemicals. Because of the fast diffusion and noticeable solubility dependence on temperature in Si [1], Ni precipitation can easily occur in Ni-contaminated Si during cooling from the high temperatures, and thereby decrease the lifetime of Si or the efficiency of Si-based solar cell [2].

The effect of Ni contamination on minority carrier lifetime of Si has been widely investigated. It was firstly addressed by Silverman et al. [3] in 1958 and Ghandhi et al. [4] in 1969. In the experiments of Ghandhi et al. [4], it was found that after Ni diffusion at 900 °C, the diffusion length of *n*-type Si even increased, which was supposed that the lifetime limiting impurities were segregated by the surface Ni layer or Ni precipitates. However, after Ni diffusion at 1093 °C, they found that the diffusion length fell to a very low value. In 1990s, it was reported that Ni decreased the lifetime of Si if its concentration in bulk was above $10^{11}\,cm^{-3}$ [5]. Moreover, the dependence of lifetime on Ni concentration was much stronger in *n*-type Si than in *p*-type Si, due to the much higher capture cross section of Ni-related centers for holes than for

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electrons [2]. However, up to now, few papers have been published about the effect of Ni on the lifetime of Si treated by rapid thermal processing (RTP), which is being applied broadly in the fabrication of different Si-based devices due to low cost and other advantages. Our previous work revealed that the effective minority carrier lifetime (τ_{eff}) of Ni-contaminated Czochralski (CZ) Si decreased with the RTP annealing temperature, however, it was almost insensitive of the annealing atmosphere [6].

Meanwhile, nitrogen-doped Czochralski (NCZ) Si has attracted considerable attentions in recent years due to its novel properties such as improving the mechanical strength, the internal gettering ability and the gate oxide integration of wafers [7–10]. It is well known that NCZ Si possesses nitrogen-related defects and more grown-in oxygen precipitates than CZ Si does [8]. Whether the defects in NCZ Si will influence the recombination activity of Ni in Si is unknown.

In this article, the recombination activity of Ni in NCZ Si treated by RTP has been investigated in detail. Moreover, the weaker recombination activity of Ni in NCZ Si compared with that in CZ Si is especially focused.

2. Experiment

The samples used in the experiment were taken from ⟨1 0 0⟩ oriented, *p*-type CZ and NCZ Si wafers with the resistivity and thickness of about $10\,\Omega\cdot$cm and 675 μm, respectively. The nitrogen concentration in the NCZ Si sample was under the detection limit of Fourier transform infrared spectroscopy, however, it could be roughly estimated to be in the range of $2–4\times10^{14}\,cm^{-3}$ from the concentration of nitrogen–oxygen complexes that are electrically active and positively correlated with the nitrogen concentration [11]. Prior to the Ni contamination, the samples were chemically polished on double sides to remove the surface damage. Subsequently, a 100 nm thick Ni film was deposited on both sides of the samples by electron beam evaporation, supposing all the Ni on the surface diffusing into the bulk, the concentration of Ni in Si was higher than $10^{18}\,cm^{-3}$, the saturation solubility of Ni in Si at 1200 °C. Afterwards, Ni in-diffusion process was conducted by RTP under different conditions: (1) the NCZ Si samples were annealed at the temperatures in the range of 700–1200 °C in Ar, N_2 or O_2 atmosphere with the average cooling rate of about 20 °C/s; (2) the NCZ Si samples were subjected to the annealing at 1000 °C in Ar followed by different average cooling rates in the range of 2–20 °C/s; (3) the CZ silicon samples were annealed at the temperatures in the range of 700–1200 °C in Ar with the average cooling rate of about 20 °C/s. The above-mentioned annealing processes were used to investigate the effect of annealing conditions in terms of temperature, atmosphere and cooling rate on the lifetime of Ni-contaminated NCZ Si samples [processes (1) and (2)] and, moreover, the difference in the lifetime of Ni-contaminated CZ an NCZ Si samples [processes (1) and (3)]. It should be pointed out that at each annealing temperature, the RTP was performed for a sufficient length of time, which was approximately in the range of 50–200 s, in order that the Ni diffused throughout the samples and reached the equilibrium solubility.

Subsequently, all the samples were chemically polished to a thickness of about 600 μm. In order to passivate the sample surface, the samples were immersed into a 20 mol/l HF solution following the surface oxidation by standard RCA cleaning [12]. The τ_{eff} was measured by Semilab WT-2000 microwave photoconductivity decay (μ-PCD) immediately after the samples were taken out of the above-mentioned HF solution to avoid the decay of surface passivation. The morphologies of Ni precipitates in the CZ and NCZ Si subjected to the RTP at 1000 °C in Ar, were observed by a Semilab SIRM-300 scanning infrared microscope (SIRM) after mechanical polish on one side.

3. Results and discussion

3.1. The implication of effective minority carrier lifetime (τ_{eff})

The τ_{eff} derived from the μ-PCD measurement is the characteristic time for the amount of non-equilibrium minority carrier decreasing to $1/e$ of its maximum, which strongly depends on the recombination channels for the excess carriers. Moreover, the decay of excess carriers mainly includes the following two main parallel processes until the thermal equilibrium is reached: (1) bulk recombination; (2) carrier diffusion to the sample surface and then surface recombination. Accordingly, the τ_{eff} is composed of bulk lifetime (τ_{bulk}) and surface lifetime (τ_{surf}), which can be presented as following [13]:

$$\frac{1}{\tau_{eff}}=\frac{1}{\tau_{bulk}}+\frac{1}{\tau_{diff}+\tau_{surf}}, \quad (1)$$