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Phosphorus diffusion in germanium following implantation and excimer laser annealing

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ABSTRACT

We focus our study on phosphorus diffusion in ion-implanted germanium after excimer laser annealing (ELA). An analytical model of laser annealing process is developed to predict the temperature profile and the melted depth in Ge. Based on the heat calculation of ELA, a phosphorus diffusion model has been proposed to predict the dopant profiles in Ge after ELA and fit SIMS profiles perfectly. A comparison between the current–voltage characteristics of Ge n^+/p junctions formed by ELA at 250 mJ/cm^2 and rapid thermal annealing at 650 °C for 15 s has been made, suggesting that ELA is promising for high performance Ge n^+/p junctions.

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1. Introduction

Innovative device design and new materials are currently being investigated because of the approaching limit for downscaling CMOS technology. Germanium has several desirable material properties that silicon does not including a band gap suitable for absorption of light at communication wavelengths (1.3–1.55 μm) [1] and an exceptionally fast low field hole mobility. So the renewed interest in Ge-based electronic devices has stimulated intensive experimental and theoretical studies. However, critical issues concerning diffusion and activation of dopants in Ge need to be considered for the feasibility of germanium as the next generation semiconductor material [2–6]. Recently, both shallow junction and high electrical activation have been realized for p-type doping in Ge [7–10]. But the heavy n-type doping is very difficult to be obtained because of the fast diffusion and limited solid solubility of n-type dopants in Ge [11]. Many research efforts have been devoted to obtain high n^+ electrical activation for Ge in the past. Whatever *in situ* doping [12], or ion implantation plus conventional annealing methods such as furnace annealing [13], rapid thermal annealing (RTA) [14], and millisecond flash annealing [15] is hard to achieve the goal of few diffusion and high doping level of n-type dopants in germanium.

Excimer laser annealing (ELA) of ion-implanted Ge has received widespread interests for its possible application in semiconductor device design and advanced CMOS technology. The technique of ELA offers many advantages compared to other thermal annealing procedures [13–15]. For example, ELA is a metastable process lasting for a few microseconds to nanoseconds in which dopants can be frozen in the substitutional sites well above the solid solubility limit [16]. And due to the low melting point of Ge, ELA is very efficient for recrystallization of ion-implanted Ge substrate at lower laser energy density as compared to silicon. Recently, combining ion implantation and excimer laser annealing, a defect-free Ge material with a high electrical activation efficiency and step-like shallow junction had been obtained [17].

Implantation and dopant activation are crucial steps for the fabrication of device structures. Nevertheless, implantation of high mass impurities can heavily damage Ge, even leading to surface swelling [17]. Phosphorus implantation is preferable because other n-type dopants, such as arsenic and antimony, may create more severe damage in Ge when implanted, and they diffuse much faster than phosphorus [11]. A lot of studies had been done to explain the dopant diffusion behavior in ion-implanted Ge [18,19]. However, to our knowledge, very few research [20] had been done about phosphorus diffusion behavior and electrical activation induced by ELA in Ge. A powerful implementation of this approach requires a full comprehension of all the phenomena occurring when Ge undergoes laser irradiation.

In this work, phosphorous implantation in Ge was carried out followed by excimer laser annealing (ELA). We aimed to study the dynamics of heat diffusion in Ge during laser annealing and the effect of ELA on phosphorus redistribution. A diffusion model has been proposed to predict the P redistribution induced by the ELA process and the model is used to fit the SIMS profiles. By using two different annealing methods of RTA and ELA technique, Ge n^+/p junctions were formed and characterized, respectively.

2. Experiments

A Ga-doped p-type Ge wafer, which is 498 μm thick, (1 0 0)-oriented, and with a resistivity of 0.088 Ω cm, was obtained from Umicore. The Ge wafer was circularly degreased in an ultrasonic bath of acetone and ethanol, and then immersed in hydrofluoric acid solution ($HF:H_2O$ = 1:50) to remove the native oxide, finally rinsed with deionized water, and blown dry by nitrogen. Prior to ion implantation, a 15 nm SiO_2 film was deposited on Ge surface by plasma enhanced chemical vapor deposition. Phosphorus was

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implanted at energy of 30 keV and a dose of 3.18×10^{15} cm^{-2} at room temperature, with a tilting angle of 7°. Before annealing, SiO_2 on the surface was removed using concentrated hydrofluoric acid HF at room temperature. Two pulses post-implantation laser annealing was performed using a 248 nm KrF excimer laser with a repetition frequency of 1 Hz and pulse duration of 25 ns, equipped with a beam forming a 4×3 mm^2 spot on samples, with energy densities from 200 to 500 mJ/cm^2. The ELA processes were performed in nitrogen ambient. The dopant profiles were measured by secondary-ion-mass spectrometry (SIMS) and crystalline quality of Ge were characterized by Raman spectroscopy. The Ge n^+/p junction diodes were formed by using ELA with an optimized energy density of 250 mJ/cm^2 and RTA (650 °C – 15 s) respectively. The patterns of Al contacts for the diodes were defined by standard photolithography and dry/wet etching with oxide hard masks. A 300 nm Al film was sputtered on the backside of Ge wafer as the other electrode. And then, I-V characteristics of Ge n^+/p junction diodes were measured.

3. Results and discussion

During the laser annealing processes, we can assume that the photon energy is locally and instantaneously converted into heat because of the fast electron-photon energy transfer (~10^{-11} s). When irradiating germanium with laser light at a sufficient energy density, a melted zone is formed in the material. As the pulse is highly monoenergetic, the melted zone is well defined and a sharp transition between the liquid and solid phase is formed. Moreover, we can assume that the irradiative heat loss at the surface is negligible and that the beam diameter is larger than the absorption length (about 6.3 nm at wavelength equal to 248 nm). Assuming that the lateral heat diffusion can be neglected, the process is described by the one-dimensional heat diffusion differential equation [21–23] as follows:

$$C(T)\rho\frac{\partial T}{\partial t} = \alpha(1-R)I_0(t)\exp^{-\alpha x} + \frac{\partial}{\partial x}\left(K(T)\frac{\partial T}{\partial x}\right), \quad (1)$$

where ρ is the density, $C(T)$ is the specific heat, α is the absorption coefficient here supposed dependent on the wavelength only, $K(T)$ is the thermal conductivity, $I_0(t)$ is the Gaussian laser pulse having a FWHM duration time (25 ns), R is the reflectivity, and $T = T(x,t)$ is the temperature. The initial condition is $T(x,0) = T_0$, which represents the substrate temperature before the irradiation. The boundary condition:

$$K_s\left.\frac{\partial T}{\partial x}\right|_{x_B} - K_l\left.\frac{\partial T}{\partial x}\right|_{x_B} = L\frac{dx_B}{dt}, \quad (2)$$

$$x = 0, \quad \frac{\partial T}{\partial x} = 0, \quad (3)$$

$$x \to \infty, \quad T = T_0, \quad (4)$$

In Eqs. (2)–(4), j is either s for solid state or l for liquid state, L is the latent heat of melting, and x_B is the liquid–solid interface position. The Eq. (2) represents the heat transportation when germanium material changes from solid phase into the liquid phase. From the Eq. (3), we consider that the irradiative heat loss at the surface can be neglected. The thermodynamical and optical data used in the heat flow calculation come from the references [24–28], as shown in Table 1.

From the heat flow calculation, several parameters such as the depth of the molten layer, the melting duration and surface temperature of the samples can be evaluated as a function of laser fluence. The calculation shows that the semiconductor surface ($x = 0$) temperature T_S rises rapidly during the laser pulse while the heat begins to diffuse into the solid. As the surface melts, T_S continues to increase and the melt boundary x_B propagates rapidly toward substrate. After x_B reaches its maximum, heat continues to diffuse into the solid and x_B decreases to zero over a time which can be as long as several microseconds. Fig. 1(a) and (b) shows the sample surface temperatures *vs.* time and maximum temperature *vs.* depth at various laser energy densities from 200 to 500 mJ/cm^2, respectively. The melting temperature threshold (melt point) for germanium is marked with horizontal dash line. The melted depth and melting duration at various energy densities are extracted and plotted in Fig. 2. The melting duration time of the surface and melted depth increase with laser energy density in the range of 200–500 mJ/cm^2.

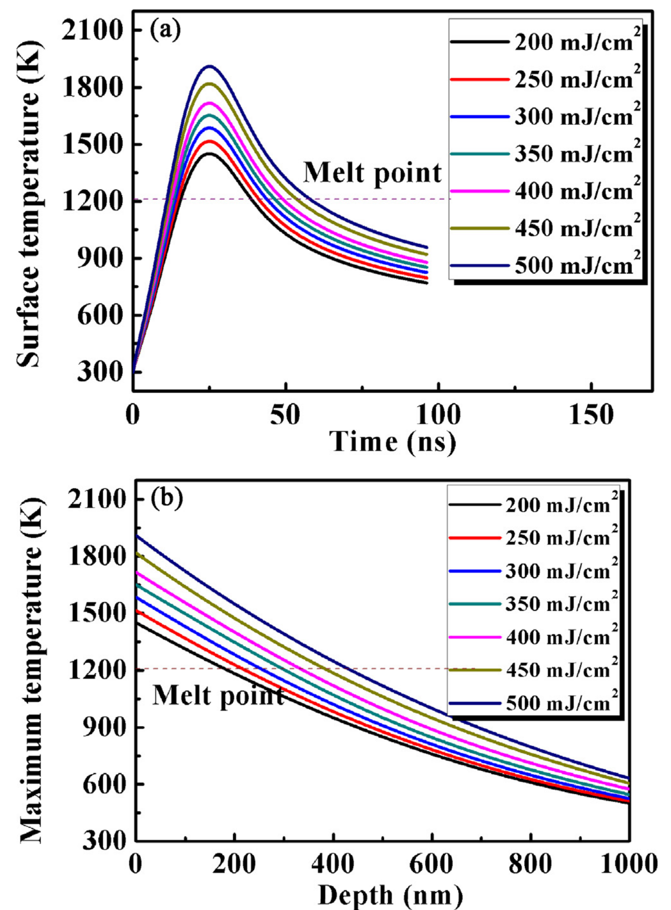

Fig. 1. (a) Simulated surface temperature as a function of time for the applied ELA energy densities. (b) Simulated maximum temperature reached as a function of depth for the applied ELA energy densities. The energy density used for simulations varies from 200 to 500 mJ/cm^2.

For the sake of explaining the diffusion behavior of phosphorus during melting and regrowth, a model considering the melted depth and melting duration (taking the values from Figs. 1 and 2 have been proposed. In the model, the standard diffusion equations with average diffusivity coefficients D_l and D_s in the liquid and solid Ge materials are included. During the ELA process, the dopant concentration $C(x,t)$ evolves according to the one-dimensional diffusion equation:

$$\frac{\partial C(x,t)}{\partial t} = D_j\frac{\partial}{\partial x}\left(\frac{\partial C(x,t)}{\partial x}\right), \quad (5)$$

where D_j is the diffusion coefficient for $j = l$ and s, namely liquid and solid. The initial condition is $C(x,0)$, which represents the dopant

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