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Hydrogen in amorphous Si and Ge during solid phase epitaxy

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ABSTRACT

Studies into the effect of hydrogen on the kinetics of solid phase epitaxy (SPE) in amorphous Si (a-Si) and Ge (a-Ge) are presented. During SPE, H diffuses into surface amorphous layers from the surface and segregates at the crystalline–amorphous interface. Some of the H crosses the interface and diffuses into the crystalline material where it either leaves the sample or is trapped by defects. H segregation at concentrations up to 2.3×10^{20} H/cm^3 is observed in buried pha-Si layers with the SPE rate decreasing by up to 20%. H also results in a reduction of dopant-enhanced SPE rates and is used to explain the asymmetry effects between the SPE velocity profile and the dopant concentration profile observed with shallow dopant implants. Conversely, H diffusion is enhanced by dopants in a-Si. These studies suggest that H diffusion and SPE may be mediated by the same defect. The extent of H in-diffusion into a-Ge surface layers during SPE is about one order of magnitude less that that observed for a-Si layers. This is thought to be due to the lack of a stable surface oxide on a-Ge. However, a considerably greater retarding effect on the SPE rate in a-Ge of up to 70% is observed. A single unifying model is applied to both dopant-enhanced SPE and H diffusion processes.

1. Introduction

In the fabrication of a broad range of Si and Ge complementary metal-oxide-semiconductor (CMOS) devices an amorphous layer may form through the implantation of heavy ions with keV energies. Alternatively, self-amorphization implants may be used before implantation of lighter ions in order to avoid implantation channeling. Regrowth of the crystal layer via solid phase epitaxy (SPE) has been identified as a pathway for achieving high dopant activation with a low thermal budget [1]. Stringent demands are placed on device fabrication modeling where devices must be made efficiently in order to meet the requirements of future technology nodes. Accordingly, an extensive SPE literature exists (for comprehensive reviews see Refs. [2–8]).

The velocity of the c–a interface during SPE has a strong dependence on many parameters, all of which need to be known for process modeling to be accurate. These parameters include the substrate crystallographic orientation [9], pressure [10], and the presence of dopants [6]. SPE is also thermally activated, the c–a interface velocity being described by an Arrhenius-type equation of the form,

$$v = v_o \exp(-E_a / kT) \tag{1}$$

where v_o and E_a are the pre-exponential factor and activation energy, respectively. For SPE in Si, $v_o = 4.64\times10^8$ cm/s and $E_a = 2.7$ eV has been determined up to the melting point [3]. The corresponding Ge values are $v_o = 2.6\times10^9$ cm/s and $E_a = 2.15$ eV determined in a temperature range of 300–540 °C [7]. The SPE rate is often unknowingly retarded by the presence of non-doping impurities such as hydrogen [4]. Hydrogen is an interesting case as it is often present during SPE unless special steps are taken. The behaviour of H during SPE then will also need to be understood and incorporated into fabrication models.

During thermal treatments on surface a-Si layers, H diffuses from the native oxide into the layer. Once the H meets the c–a interface it strongly segregates in the amorphous phase and retards the SPE rate by up to ~50% [4]. This in-diffusion occurs whenever there is water vapor in the ambient or a surface oxide present. For thin a-Si layers (<400 nm), such as those produced during shallow junction processing, a nearly constant concentration of ~2×10^9 H/cm is expected at the c–a interface throughout the SPE process [4]. Amorphous layers formed by cluster implantation of decaborane ($B_{10}H_{14}$) [11] also contain H and therefore may affect the SPE rate.

For thick a-Si layers, H can infiltrate several microns into the a-Si layer before meeting the c–a interface. The SPE rate is found to decrease linearly with H concentration up to $[H]\approx3\times10^{19}$ cm^{-3}. For greater concentrations up to 7×10^{19} cm^{-3} the SPE rate depends only weakly on the H concentration. This threshold value has been correlated with the density of dangling bonds (DB) in a-Si formed by ion implantation and has been cited as evidence for the possible involvement of DBs in the SPE process [4,12].

Hydrogen diffusion is also thermally activated and for low H concentrations ([H]) has been described by an equation similar to

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Eq. (1) with v and v_o replaced by a pre-exponential factor, $D_o = 2.2\times10^4\,\mathrm{cm^2/s}$ and an activation energy $E_a = 2.7$ eV [13]. Since a common activation energy is shared by SPE and H diffusion, one is led to suspect that the rate limiting step in these two seemingly unrelated processes may be the same [13]. Hence, studies into H diffusion and its role during SPE can also provide important insight into the SPE mechanism.

In this paper, experiments concerning the role of H during SPE are presented. Firstly, H implantation into buried a-Si layers is used to study the SPE retardation at H concentrations greater than $7\times10^{19}\,\mathrm{cm^{-3}}$. H is also shown to have a temperature dependent segregation coefficient. The interaction of H with dopants is also observed through SPE and H diffusion studies presented here. The presence of dopants can enhance the diffusion of both H in-diffusing from the surface and implanted H. The SPE rates in a-Ge are also shown to suffer from H contamination. These observations are drawn together into a single model, the generalized Fermi level shifting model, which links structural changes at the interface or H diffusion to the local electronic structure [6,10]. The impact of these results on device modeling for fabrication processes is considered.

2. Theoretical background

The generalized Fermi level shifting (GFLS) model is used in this work to describe the effect of H on SPE and dopant-enhanced SPE and H diffusion. The GFLS model has been successful in describing the dopant dependence of SPE in both a-Si and a-Ge [6,7,10]. The effect of pressure has also been recently incorporated into the model [14].

According to the model, the number of events, R, is determined by the concentration of neutral defects, X^0 and its positively or negatively charged counterparts, $X^{\pm}$. The events could be either the transport of H from one site to another or the rearrangement of an atom at the c–a interface in SPE. It is assumed that the defects are in thermal and electronic equilibrium determined by the local band structure density of states. The event is then expected to be proportional to the concentration of these defects. For an n-type semiconductor and its intrinsic counterpart the rate of the event is given by

$$R = \alpha([X^0] + [X^-]|_{\mathrm{doped}}) \tag{2a}$$

and

$$R_i = \alpha([X^0] + [X^-]|_{\mathrm{intrinsic}}) \tag{2b}$$

respectively, where α is a constant and the square brackets denote a concentration. The charged fraction of defects is determined by Fermi–Dirac statistics and, for an n-type semiconductor, is expressed as the ratio of charged to neutral defect concentrations,

$$\frac{[X^-]|_{\mathrm{doped}}}{[X^0]} = g^- \exp\left(\frac{E_f - E^-}{kT}\right) \tag{3}$$

where E_f is the Fermi level and E^- represents the energy level within the band gap of the defect X^-. If a DB defect is responsible for the SPE process then it is expected that the degeneracy is $g^- = 1/2$ and $g^+ = 1$ for n-type and p-type semiconductors, respectively [6].

Once Eq. (3) is substituted into Eq. (2) we obtain,

$$\frac{R}{R_i} = \frac{1 + \frac{[X^-]}{[X^0]}|_{\mathrm{doped}}}{1 + \frac{[X^-]}{[X^0]}|_{\mathrm{intrinsic}}} = \frac{1 + g^- \exp\left(\frac{E_f - E^-}{kT}\right)}{1 + g^- \exp\left(\frac{E_{fi} - E^-}{kT}\right)}. \tag{4}$$

This equation is used to fit the normalized SPE rates (v/v_i) or H diffusion coefficient (D/D_i) data as a function of temperature with g and E^- being free parameters.

We now consider the effect of H at the c–a interface. A number of studies have suggested that H retards SPE through the passivation of DBs at the c–a interface thus reducing the number of crystallization sites available [4,12]. According to the GFLS model, the defect concentration would become $[X_h^0] = [X^0] - a[H]$. The charged defect is reduced by an amount $b[H]$ where a and b represent the fraction of H that passivates the neutral and charged defects, respectively. Eq. (4) then becomes

$$\frac{v}{v_i} = \left(1 - \frac{a[H]}{[X^0]}\right)\left[\frac{1 + \frac{[X_h^-]}{[X_h^0]}}{1 + \frac{[X^-]}{[X^0]}}\right] \tag{5}$$

where v and v_i are the dopant/H-affected and intrinsic SPE velocities, respectively. The term in square brackets is the normalized rate enhancement due to doping. The first term in parentheses has a linear trend with [H]. Indeed, the SPE retardation is observed to have a linear dependence on [H] up to a concentration of $3\times10^{19}\,\mathrm{H/cm^3}$ where the normalized SPE rate is about 0.5 [4]. For the case without dopants ($E_f = E_i$), the dopant term is expected to be close to unity since $[X^-]/[X^0] \approx 0$ determined from Eq. (3). Therefore, the factor $[X^0]/\alpha \approx 6\times10^{19}\,\mathrm{H/cm^3}$. This is close to the value of $1.5\times10^{20}\,\mathrm{H/cm^3}$ reported by Oberlin et al. [12]. Furthermore, H is found to reduce the pre-exponential factor in Eq. (1) but not the activation energy, suggesting that H passivates crystallization sites while not affecting the energy associated with a crystallization event [7,15]. Various studies are described in the following sections to test this model and develop a more complete understanding of the role of H during SPE.

3. Experiment

3.1. Sample preparation

The kinetics of SPE were measured in amorphous layers formed by self-ion implantation into <100> wafers. A National Electrostatics Corp. 1.7 MV tandem accelerator was used for all implants. The samples were tilted 7° off the incident beam axis to avoid channeling and also rotated about the surface normal by a similar amount to prevent any remaining possibility of planar channeling [16]. Substrates were affixed with Ag paste to the implanter stage, which was held at 77 K. Good thermal contact was especially important for a-Ge formation in order to avoid the porous structure that forms in high-fluence room temperature implanted Ge [17,18]. Multiple ion beam energies were chosen to form homogeneous amorphous layers ranging between 1.5 and 4.2 µm thick.

3.2. Time resolved reflectivity

The SPE rates of the c–a interface were determined from time resolved reflectivity (TRR) measurements by acquiring reflectivity data simultaneously using two HeNe lasers at wavelengths of $\lambda = 1.152$ µm to probe the thin amorphous layers and at $\lambda = 1.523$ µm for the thicker layers. As the c–a interface moves through the sample, peaks in the TRR reflectivity trace occur every $\lambda/2n$. By combining the measured TRR traces and a theoretical reflectivity versus c–a interface position curve the velocity of the interface was determined. These data were collected while the samples were held on a resistively heated vacuum chuck and annealed in air over the temperature range of 460–660 °C for Si and 300–540 °C for Ge. The temperature of the samples during the anneals was calibrated by comparing the reading of a type-K thermocouple embedded in the sample stage with the melting points of various suitably encapsulated metal films evaporated onto Si wafers. The error associated with the temperature reading was found to be ±1 °C. Measurements were performed in air to match the experimental conditions of other studies and so that the effects of H infiltration could