Low-temperature germanium thin films on silicon

Vito Sorianello,1 Lorenzo Colace,1 Nicola Armani,2 Francesca Rossi,2 Claudio Ferrari,2 Laura Lazzarini,2 and Gaetano Assanto1

1Nonlinear Optics and OptoElectronics Lab (NooEL), Via della Vasca Navale 84, 00146 Rome, Italy
2Institute IMEM-CNR, Parco Area delle Scienze 37/A, 43124 Parma, Italy

Abstract: We discuss thermal evaporation of Germanium thin films as a suitable route to realizing near-infrared detectors integrated on a Silicon platform. We study the structural properties of samples grown at various substrate temperatures by X-ray diffraction and transmission electron microscopy, showing that Ge thin films are amorphous when deposited below 225°C, mono-crystalline between 225 and 400°C, poly-crystalline above 450°C. We further investigate their optical and electrical properties using differential optical absorption spectroscopy, Hall and photocurrent measurements. Finally, with the evaporated Ge thin films we demonstrate near-infrared photodiodes with low dark current density and good responsivity at 1.55 µm.

©2011 Optical Society of America

OCIS codes: (310.1860) Deposition and fabrication; (310.3840) Materials and process characterization; (160.6000) Semiconductor materials; (160.1890) Detector materials.

References and links


#149193 - $15.00 USD

Received 13 Jun 2011; revised 20 Jul 2011; accepted 3 Aug 2011; published 5 Aug 2011

©2011 OSA

1 September 2011 / Vol. 1, No. 5 / OPTICAL MATERIALS EXPRESS 856
1. Introduction

In recent years, Silicon photonics has gained a leading role in applied physics and optical engineering [1]. To date, several photonic and optoelectronic components have been successfully integrated on a Silicon platform exploiting several processes of the standard microelectronics industry [2]. However, the challenge of integration is still open because of the technological problems that prevent a viable monolithic integration of near-infrared (NIR) sensing devices with Si electronics. In fact, while Silicon is an indirect bandgap semiconductor transparent at NIR communication wavelengths, NIR laser sources and detectors require smaller bandgap materials, mostly III-V compounds which are essentially incompatible for integration with standard Si technologies. In this context, Germanium-on-Silicon has been recognized as the best alternative towards the monolithic integration of NIR detectors on Silicon platforms, with high performance Ge-on-Si detectors recently demonstrated [3,4]. Nonetheless, the monolithic integration of Ge photodiodes with standard Si electronics is still hindered by compatibility issues, i.e., thermal budget and cross-contamination stemming from Ge deposition. Although several Ge-on-Si deposition techniques have been successfully implemented, most of them require high temperatures which can hardly coexist with standard CMOS technology [5]. Recently, we have proposed physical vapor deposition of Ge on Si by thermal evaporation (TE) as a viable low-temperature growth process and demonstrated optoelectronics devices by integrating Ge-on-Si photodetectors with either CMOS circuitry [6] or Silicon photonics elements [7]. However, a detailed analysis and understanding of TE Germanium thin films on Si is still lacking.

In this Paper we report a comprehensive characterization of structural, optical and electrical properties of Ge thin films thermally evaporated on Si. We show hereby that, by simply controlling the substrate temperature, it is possible to grow Ge thin films of different crystalline qualities, obtaining mono-crystalline epitaxial Ge at temperatures in the range 250-400°C. Finally, we discuss this approach towards fabricating efficient NIR detectors for Si optoelectronics.

2. Deposition details

Ge thin films were grown on Si by thermal evaporation in a vacuum chamber with a background pressure of $10^{-8}$ Torr and about $10^{-7}$ Torr during deposition. The material source was high purity (99.999%) small grains of Ge in a tungsten crucible; the substrates were either (100) Silicon or Silicon-on-Insulator (SOI) wafers, carefully cleaned in a standard RCA solution. Prior to Ge deposition, the native silicon-oxide was removed from the substrate surface by chemical etching with buffered hydrofluoric acid (buffered oxide etching - BOE); this pre-TE treatment was a crucial step in obtaining crystalline films. Besides removing the native oxide, BOE also played the important role of passivating the Si surface by terminating the dangling bonds with hydrogen-ions; an H-passivated surface is chemically robust and resistant to oxidation, permitting to handle the specimens in air before placing them in a
vacuum. During deposition the evaporation rate was kept constant at about 2 Å/s, whereas the substrate temperatures could be adjusted from 200 to 500°C.

3. Film characterization

3.1 Structural properties

We investigated the structural properties of Ge films by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD analysis of the (004) planes of both Si and Ge was performed in a high resolution (HR) diffractometer. Figure 1(a) displays the HR-XRD ω–2θ scans of the 200 nm Ge films evaporated on Si at various temperatures. The scans were performed with open window geometry to show the mosaic spread of the films. The samples grown at 200°C did not exhibit any Ge diffraction peak, as expected from amorphous films; substrate heating to 250°C and above, up to 400°C, lead to the deposition of crystalline Ge films, as indicated by the presence of an intense Ge (004) peak.

![Fig. 1. (a) HR-XRD ω–2θ diffraction profile of Ge-on-Si films grown at various substrate temperatures. (b) FWHM of Ge (004) diffraction peaks versus substrate temperature.](image)

The transition from an amorphous to a crystalline phase is known to take place within this temperature interval [8]; in fact, we observed weak diffraction signals from films deposited at temperatures as low as 225°C, where amorphous Ge and crystallites should coexist. Nearly epitaxial growth can be achieved at temperatures between 225 and 400°C; beyond this limit various mechanisms cause the formation of either amorphous or highly-defected films, according to the diffusion energies of the adatoms on the substrate, strictly associated to growth temperature [9–11]. This is consistent with our observation, as the broad Ge peaks are due to the significant defect density of the film. In bulk crystals the width of the diffraction peak can be associated to the threading dislocation density [12]. In the present case the FWHM of the Ge (004) diffraction peak varies from 0.35 to 0.33 degrees in a 250-400°C interval of growth temperatures, as visible in Fig. 1(b). Other highly mismatched thin films (~4% mismatch between Ge and Si), such as GeSi/Si films with high Ge content grown by ultra high vacuum CVD [13] or InAs grown on GaAs by molecular beam epitaxy [14] at higher temperatures exhibit a 004 peak with FWHM of several hundredths arcseconds. As explained by Kaganer [15], in these films the peak broadening is mainly due to the quite irregular network of misfit dislocations at the interface, generating local tilt of the lattice planes. In our samples the larger FWHM is probably caused by a high density of threading dislocations associated with the growth mode at low temperature; nevertheless, peak broadening in these evaporated samples requires a more in-depth investigation which will be reported in a forthcoming publication.
Although XRD profiles do not vary significantly when the substrate temperature is raised up to 400°C, at 450°C the Ge (004) intensity peak starts reducing and is much lower at 500°C. Such decrease is associated to the transition from a mono-oriented to a poly-oriented crystal, as also supported by the large angle ω–2θ XRD diffraction profiles visible in Fig. 2.

Fig. 2. XRD large angle scan of Ge-on-Si films grown at 300 (blue) and 500°C (red).

Ge grown at 300°C exhibits a single intense Ge (004) peak, suggesting a single crystal structure; films at 500°C display several extra peaks characteristic of other crystalline planes (111, 220, 113). This transition to poly-oriented structures at temperatures > 450°C is unexpected and we speculate it to be associated to a different growth mode of the layer. At temperatures < 450°C the growth of Ge on Si proceeds layer-by-layer with strain relaxation occurring by nucleation of misfit dislocations rather than island formation [10]. In such conditions the samples present misfit dislocations as well as very small pyramidal stacking faults at the Ge/Si interface and threading dislocations propagating all across the Ge thickness; TE films at 500°C display a more complex defect structure. Nevertheless, films prepared below 450°C exhibit smooth surfaces, whereas at higher temperatures have a pronounced surface roughening. This varying morphology is apparent in Fig. 3, showing TEM cross sections of samples prepared at 300 (Fig. 3(a)) and 500°C (Fig. 3(b)). For each sample, the top image is acquired in Scanning TEM-High Angle Annular Dark Field (STEM-HAADF) mode, the bottom image in conventional Bright Field (BF) mode. The contrast in STEM-HAADF mode is essentially an atomic number contrast [16], so that the Ge film is immediately imaged as a brighter layer on top of the Si substrate with lower atomic number. Conversely, the diffraction contrast is dominant in the conventional TEM-BF mode, allowing to image the defects both at the interface and within the thin film. We believe that between 450 and 500°C the growth mode changes from 2D to 3D (Stranski-Krastanov) with the formation of columnar structures of multiple orientations [17]. We measured an rms film roughness of about 1 nm at lower temperatures, which increased to tens of nanometers at 500°C.

In order to further investigate the structural properties of both mono- and poly-crystalline TE samples we resorted to high-resolution (HR) TEM. The results are displayed in Fig. 4 with the insets showing the Fourier transforms (FT) of the HR images. While Ge layers at 300°C are mono-crystalline (epitaxial), those at 500°C have diffractograms typical of a polycrystalline structure, possibly columnar with individual columns differently oriented. We evaluated the intensity distribution of the FT spatial frequencies in order to determine which region corresponded to a particular frequency; the results in Fig. 5 clearly indicate that the Ge layer is structured in columns.
Fig. 3. Cross-sectional TEM images of samples grown at (a) 300°C and (b) 500°C: the STEM-HAADF image is shown upward, the BF image downward. The difference in surface morphology is apparent.

Fig. 4. Cross-sectional HR TEM in [011] zone axis of samples evaporated (a) at 300 °C and (b) at 500 °C. The insets show the Fourier transforms.
3.2 Optical and electrical properties

We measured the near-infrared (1200-1650 nm) absorption spectra of amorphous and epitaxial Ge films on Si using differential optical absorption spectroscopy [18] and compared them with reference bulk Ge [19], as Fig. 6 shows. The amorphous Ge films exhibit an optical absorption slowly decreasing with wavelength without any specific features in the proximity of the Ge bandgap. The spectra of epitaxial Ge films are comparable with those from bulk Ge up to the cutoff wavelength, namely 1550 nm. At longer wavelengths bulk Ge shows the sharp transition corresponding to its direct bandgap (about 0.8 eV), whereas the TE thin film spectra have a smooth variation, attributed to the high dislocation density. In particular, dislocations introduce electronic levels in the forbidden bandgap available for energy transitions [20]; when the photon energy is comparable with the gap between the valence band and the dislocation levels, some photons are still absorbed. In addition, the measurement reliability worsens beyond the gap as the increased transparency eases a number of multiple reflections in the film thickness. The results demonstrate that both amorphous and crystalline evaporated Ge films have significant NIR absorption and can be employed for light detection. However, as we demonstrated earlier [21], the transport properties of the TE amorphous Ge are not well suited for realizing optoelectronic devices.
We also studied the electrical properties of Ge films on Si at temperatures between 300 and 500°C. At room temperature we employed the Hall effect to determine the majority carrier type, concentration and mobility; Hall bars were fabricated by standard optical lithography on the Ge films evaporated on low doping n-type Silicon-on-Insulator wafers with a 220nm Si overlayer to prevent shunt effects; the external contacts consisted of a double layer of chromium and gold defined by lift-off. All samples show transport properties dominated by holes, although no intentional doping was introduced. The p-type behavior of Ge films on Si was previously reported by other groups using different growth techniques [22,23] and is associated to structural defects, namely dislocations, creating acceptor levels in the forbidden gap near the valence band [20]. The epitaxial films exhibit a large hole concentration with a small increase from 3·10^{17} cm^{-3} when grown at 300°C to 5·10^{17} cm^{-3} at 400°C. Unfortunately, the hole mobility is strongly affected by dislocations, as well, with values going from 83cm^{2}/Vs in films TE at 300°C to 57 cm^{2}/Vs in those deposited at 400°C. Such mobilities are about ten times lower than those in bulk Ge with comparable doping and stem from the scattering of majority carriers at each dislocation core [20,24]. Temperatures above 400°C worsen the electrical properties due to the formation of poly-crystalline films. The latter exhibit the same p-type behavior with hole concentrations of about 2·10^{18} cm^{-3} and mobilities < 30cm^{2}/Vs. These poorer properties are associated to recombination mechanisms at the grain boundaries [25].

We measured the photocurrent to evaluate the diffusion length of minority carriers in TE Ge films; to this extent we fabricated simple pn junction photodiodes by depositing 200nm Ge films (p-type) on n-type (1-3 Ωcm) Si wafers and defining square-mesas by standard optical lithography. The contacts, realized by lift-off to avoid damages of the illuminated surface, consist of a double layer of chromium and gold; the top contact was equipped with a large window to allow illumination at normal incidence. The diffusion length of minority carriers could be evaluated by fitting the responsivity versus reverse bias with the expression [16]:

\[
R(V) = \frac{\lambda}{1.24} \left(1 - \Theta\right) \left(1 - \frac{e^{-\alpha x(V)}}{1 + \alpha L_n}\right)
\]

where \(\lambda\) is the wavelength in micrometers, \(\Theta\) the Fresnel reflection at the Ge surface, \(\alpha\) the optical absorption coefficient, \(x(V)\) the voltage-dependent depletion region in Ge and \(L_n\) the diffusion length for minority carriers. Assuming a Ge refractive index of 4.2 at 1.55 \(\mu\)m, we evaluated the depletion region versus reverse bias based on the Hall measurements. Figure 7 shows the diffusion lengths of minority carriers versus growth temperature compared to the mobilities of majority carriers. Epitaxial films have short diffusion lengths from about 32 nm (at 300°C) to 16nm (at 400°C), while polycrystalline films exhibit even shorter diffusion lengths down to about 9nm at 500°C. This is associated to larger dislocation densities versus increasing temperatures up to the formation of polycrystalline films. In fact, dislocations and grain boundaries in epitaxial and polycrystalline films, respectively, act as traps for electrons and reduce their mean free path before recombination [20].
The consistency of diffusion length and mobility data versus temperature confirms the best TE conditions at 300°C. Achieving the best transport characteristics at a low growth temperature is crucial for the integration of these films with standard CMOS processes. While large hole concentrations and low mobilities limit the use of evaporated Ge films in high performance minority carrier devices (i.e. bipolar transistors), they can be well exploited in properly designed NIR detectors.

4. NIR photodetectors

We fabricated both normal incidence and guided-wave photodiodes and characterized them in terms of dark current density $J_d$ and responsivity $R$ at 1.55 µm. Figure 8(a) shows the typical $J_d-V$ and $R-V$ curves of normal incidence diodes (sketched in Fig. 8(b)) realized with TE Ge at 300°C versus reverse bias. These devices exhibit good rectifying $J_d-V$ characteristics with typical dark current densities of about 2 mA/cm$^2$ in reverse bias at 1V, among the lowest ever reported in literature for Ge-on-Si NIR photodectors [26].

The 1.55µm responsivity varies slowly versus bias with a high figure even in the photovoltaic regime. This is noteworthy and confirms the good collection properties despite the fact that in the detector the active layer is close to the highly defected Ge/Si interface. However, the sensitivity is low owing to the limited active absorption region in Ge. As shown in Eq. (1), in fact, the responsivity depends on the width of the depleted zone in Ge and on the diffusion length of minority carriers. Since the high (effective) p-type Ge doping limits depletion to a few nanometers (we calculated a depleted region of about 7nm at 1V reverse), the photogeneration properties in normal incidence photodiodes are hindered by a short active absorption layer of only tens of nanometers. The drawback above can be eliminated by employing guided-wave geometries where the incident light can propagate along the junction plane [27]; hence, absorption can be maximized by properly designing length and thickness of the waveguide. To fabricate waveguide photodetectors we evaporated Ge thin films on SOI at 300°C, with 100µm length to achieve full absorption of the propagating mode. Figure 9 shows their typical responsivity at 1.55µm and dark current density, together with a schematic drawing of the device: the 10mA/cm$^2$ dark current density at 1V reverse is one order of magnitude higher than in normal incidence detectors, but still among the lowest in literature. Conversely, the 1.55µm responsivity is more than two orders of magnitude higher, exceeding 0.22 A/W at a reverse bias of 1V. In order to further improve the device performance both for
normal incidence and in guided wave geometries, the depletion layer width has to be increased by resorting, for instance, to doping compensation. In this case a larger thermal budget could become necessary.

![Graph](image)

Fig. 8. (a) Dark current density and 1.55µm responsivity versus reverse bias for normal incidence Ge-on-Si photodetectors fabricated at 300°C. (b) Schematic top and side views of the device.

![Graph](image)

Fig. 9. (a) Dark current density and 1.55µm responsivity versus reverse bias in Ge-on-SOI waveguide photodetectors fabricated at 300°C. (b) Schematic side and top views of the device.

5. Conclusions

In conclusion, we studied the structural and optoelectronic properties of Ge on Si thin films grown by thermal evaporation at substrate temperatures in the range 200-500°C. Films deposited below 250°C are amorphous; above 250°C but below 450°C exhibit a monocrystalline epitaxial structure with large dislocation densities stemming from lattice relaxation; above 450°C become poly-crystalline. In the interval 300-400°C suitable for epitaxial growth, the best structural properties can be obtained by TE at 300°C.
We characterized the evaporated films in terms of optical and electrical properties. The NIR optical absorption of the epitaxial films is comparable to bulk Ge below the cutoff wavelength. A large defect density affects the electrical properties, causing a significant albeit unintentional $p$-type doping owing to the acceptor levels introduced by dislocations; a large hole concentration impairs the transport properties, i.e. mobility and diffusion length of minority carriers. Even from the electrical standpoint, however, the best films seem to be those prepared at 300°C, with typical hole concentrations of about $10^{17}\text{cm}^{-3}$, mobility of 80cm$^2$/Vs and diffusion length of 30nm for minority carriers.

We employed these low-temperature TE films for the realization of Ge-on-Si NIR detectors, in order to demonstrate the process suitability towards back-end integration in a standard CMOS flow in Silicon foundries. We demonstrated normal incidence Ge-on-Si detectors with very low dark current density (2mA/cm$^2$) and good responsivity of 2.2mA/W (1V reverse) at 1.55µm, as well as guided-wave Ge-on-SOI photodiodes with low dark current density (10mA/cm$^2$) and 1.55µm responsivity >220mA/W.