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Investigation of crystallized germanium thin films and germanium/silicon heterojunction devices for optoelectronic applications



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ABSTRACT

Crystallization of germanium (Ge) thin films was investigated by depositing Ge on glass and silicon substrates using electron beam (e-Beam) evaporation. The hole carrier concentration in Ge thin films deposited on glass substrates was found to decrease slightly with increasing annealing temperature, whereas its Hall mobility was found to increase monotonically. For all crystallized Ge thin films herein reported, the conductivity was found to be dominated by holes (p-type). This characteristic was then exploited to fabricate p-Ge/n-Si heterojunction diodes on n-type silicon substrates, which were then investigated by analysis of their current-voltage and capacitance-voltage characteristics. It was found that increasing annealing temperatures lead to significant improvements in on/off ratio and ideality factor, as well as increased built-in voltage. After crystallization of the top p-Ge layer through annealing at 600 °C, the devices indicated an on/off ratio of 10⁶, an ideality factor of 1.25 and a built-in potential of 0.58 eV. The improvement in device performance is correlated with the crystallization of the Ge thin films, as confirmed by Hall effect and X-ray diffraction measurement, which indicated increases in hole mobility and improved solid-phase crystallization with increases in annealing temperature. The photoresponse of the devices was characterized employing a two-dimensional mapping approach, which provides insight into the optical generation and recombination processes at the Ge/Si heterojunction. The results herein presented indicate that thermally crystallized Ge thin films may be of significant promise for electronic and optoelectronic device applications.

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1. Introduction

Germanium is a relatively well-understood semiconductor material owing to several decades of research [1–5], and has recently experienced renewed interest as a mobilityenhancement channel material for advanced MOSFET devices [6–9], and as a narrow bandgap material for near-infrared

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http://dx.doi.org/10.1016/j.mssp.2014.10.041 1369-8001/© 2014 Elsevier Ltd. All rights reserved. wavelength photodetectors [10,11]. Additionally, germanium has found widespread application as the bottom cell in multijunction solar cells because of its low energy bandgap (0.67 eV) and favorable optical absorption properties [12,13]. Despite many potential applications, the relatively high cost of crystalline germanium limits its application; however, deposited thinfilm germanium offers a promisingly cost-effective alternative [14]. Generally, solid-phase crystallization (SPC) is a simple and cost-effective method to crystallize amorphous materials on insulators such as glass [15]. The thermodynamics and kinetics of solid-phase crystallization films from amorphous phase

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have been explained by classical nucleation and growth theory. When amorphous films are annealed to a certain temperature, the film is transformed into a thermodynamically stable crystalline phase through four steps: incubation, nucleation, growth and steady state. In this process, small crystallites are formed at nucleation sites, which then grow in size with increasing time at the expense of the contiguous amorphous matrix [16]; solid-phase epitaxy (SPE) growth can be regarded as interface mediated as the rearrangement of atoms is influenced by the interface between the amorphous film and the single-crystal template [17]. Many studies have investigated SPC of germanium thin films deposited and crystallized using a variety of techniques, with most studies seeking to optimize optical and electrical properties for specific applications [3,18-24]. However, there are relatively few investigations that report the characteristics of devices fabricated using crystallized Ge thin films. In this study, amorphous and nonconductive Ge thin films evaporated employing the electronbeam (e-Beam) deposition method have been crystallized by SPC through thermal annealing at temperatures ranging from 350 °C to 600 °C. Hall-effect measurements were then employed to investigate the electronic transport parameters of the Ge thin films and optimize the crystallization process. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and optical transmission measurements were also employed to optimize thermal annealing conditions, and provide information annealing effects for Ge thin film deposited on glass and silicon substrates. For the optimized Ge crystallization process, crystallized p-Ge on n-Si heterojunction diodes were fabricated, and key device parameters, such as ideality factor and junction built-in potential, were extracted from currentvoltage (I-V) and capacitance-voltage (C-V) measurements. Device photoresponse characteristics were measured employing laser-illumination and two-dimensional (2D) photocurrent mapping.

2. Experimental techniques

For investigations of Ge thin films deposited on glass, standard microscope glass slides were cleaned in consecutive baths of acetone, methanol and isopropyl alcohol (IPA), followed by ultrasonic rinsing in warm deionized water. For the study of Ge thin films deposited on Si substrates, phosphorous-doped n-type (100) Si wafers were employed. The nominal resistivity of the Si substrates was $1-10 \Omega$ cm, which represents an intentional dopant concentration in the 4.51×10^{14} – 5.95×10^{15} cm⁻³ range. The Si substrates were solvent cleaned and then etched in a 1:10 HF:H₂O solution for 5 s to remove native oxide on the substrate surface. Following substrate preparation, Ge thin films were deposited by e-Beam evaporation employing a 99.999% pure Ge evaporation at a base background pressure of 10⁻⁶ Torr. The Ge thin films were deposited with the substrates at room temperature at an evaporation rate of 0.3 nm/s to a final thickness of 1 µm, as determined using a Dektak stylus profilometer. The deposition rate employed was optimized to yield uniform and high quality films with relatively low pinhole densities (preliminary investigations had indicated that high deposition rates results in high density of pinholes) [25]. The as-deposited Ge thin films were found to be highly reactive (and soluble

in water); thus an initial thermal annealing step was performed at 300 °C in a flowing-N₂ ambient for 30 min to stabilize the films for subsequent wet-chemical processing. The Ge thin films deposited on glass substrates were patterned into Van der Pauw structures with Greek-cross geometry employing NH₄OH:H₂O₂:H₂O (1:1:20) for mesa delineation. Resistivity and Hall-effect measurements were performed on these test-structures in an electromagnet system, wherefrom the resistivity, carrier concentration and mobility of the Ge thin films were extracted. The samples were then subjected to further annealing steps at increasing temperatures up to 600 °C in flowing N₂ ambient. The duration of each subsequent thermal annealing step was 30 min. After each subsequent thermal annealing step, the resistivity and Hall-effect measurements were repeated to quantify the effects of thermal annealing on the electronic transport parameters of the samples. Ge thin films of different thicknesses were then prepared on glass and silicon substrates which were then characterized using XRD and SEM to determine the effect of the annealing temperature on surface morphology, and qualitatively determine the extent of crystallization from 2-theta scans. Optical transmittance measurements were also performed on Ge thin films samples deposited on glass. Finally, the electrical, surface-morphological, optical and crystallographic data were used to determine optimal process parameters which were then employed to fabricate devices. Ge/Si heterojunction diodes were realized by deposition and crystallization of p-type Ge thin films on n-Si wafers. The device active area was defined using a selective Ge/Si mesa etch, and ohmic contacts were formed by thermal evaporation of 5 nm Cr followed by 50 nm Au. A finger pattern was employed to contact the crystallized Ge active area to minimize shading losses. The p-on-n devices were then characterized employing I-Vand C-V measurements, as well as 2D photocurrent mapping. The process flow outline is summarized in Fig. 1.

3. Results and discussion

3.1. Characterization of crystallized Ge thin films

Results from the analysis of resistivity and Hall-effect measurements of Ge thin films deposited on glass substrates are shown in Fig. 2, which illustrates the relationship between

Substrates cleaning and deposition of a-Germanium Crystallization by annealing in a furnace with flowing N₂ Characterization of the Ge films by various measurements Crystallizing Ge on Si & photolithography for patterning Mesa isolation etching (NH₄OH:H₂O₂:H₂O=1:1:20) Contact patterning and metallization : Crystallization of Ge films : fabrication of Ge/Si diode



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