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Laser ablation and growth of Si and Ge

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ABSTRACT

In this work, we investigated the laser ablation and deposition of Si and Ge at room temperature in vacuum by employing nanosecond lasers of 248 nm, 355 nm, 532 nm and 1064 nm. Time-integrated optical emission spectra were obtained for neutrals and ionized Ge and Si species in the plasma at laser fluences from 0.5 to 11 J/cm^2. The deposited films were characterized by using Raman spectroscopy, scanning electron microscopy and atomic force microscopy. Amorphous Si and Ge films, micron-sized crystalline droplets and nano-sized particles were deposited. The results suggested that ionized species in the plasma promote the process of subsurface implantation for both Si and Ge films while large droplets were produced from the superheated and melted layer of the target. The dependence of the properties of the materials on laser wavelength and fluence were discussed.

1. Introduction

The use of pulsed lasers in the fabrication and growth of germanium (Ge) and silicon (Si) nanomaterials and devices have recently attracted increased interest. It differs from molecular beam epitaxy, electron beam deposition or thermal evaporation, laser pulses interaction with materials and it produces plasma plume that may constitute macro particulates, atoms, neutrals, ions and clusters [1,2]. For Si and Ge, various coatings have been obtained when the plasma plume is condensed onto a substrate: amorphous or crystalline films [3–10], nanoparticles/nanoclusters [4,11–16], Ge nanoring [17], Si nanocrystals [13,18] and Ge quantum dot [19,20]. Nevertheless, the interactions of the nanosecond laser pulse with semiconducting Si and Ge resemble the interactions with metals with high thermal diffusivity; while the ns laser pulse may interact with the plasma that was formed. This results in a complex ablation, plume formation and propagation, and finally growth process that extensive and detailed studies of the growth and parameter dependency are very much needed. In addition to materials characterization, plasma diagnostic and characterization such as emission spectroscopy, time-of flight measurement, mass spectrometry, electrostatic measurement [21] can provide information on the intermediate stage of the growth process, and would be beneficial for better understanding and control of the growth process.

We explore the use of nanosecond (ns) pulsed laser-produced plasma for deposition of Ge and Si at room temperature in vacuum. By varying the laser parameters, we studied the capability and the suitability of the process for material deposition and growths. Nanosecond laser pulses which covered the range from ultra-violet to infrared were used to ablate polycrystalline Si and Ge targets. Time integrated optical emission spectra were obtained as a function of laser fluence and wavelengths for diagnostic of the ablated plasma species for both Si and Ge ablation.

2. Experimental details

A KrF excimer laser with ($\lambda_{laser}=248$ nm, 25 ns) and a Nd-YAG laser ($\lambda_{laser}=1064$ nm, 532 nm, 355 nm, 5 ns) were used for the ablation and deposition from either a polycrystalline Si or a Ge sputtering target (Kurt J. Lesker, undoped, 99.999%) in background pressure of $<10^{-4}$ Pa. The laser beam was incident at an angle of 45° onto the target. The beam was focused to a size of 0.0028 cm^2 for Nd-YAG laser, and imaged to a size of 0.007 cm^2 for KrF laser. This results in laser fluences of 1.5–10 J/cm^2 (3×10^8–2×10^9 W/cm^2) for the Nd:YAG laser and 1–3 J/cm^2 for the KrF laser. In both cases, an area of 6 mm × 6 mm was ablation, either by scanning the laser beam or moving the target stage. The area was pre-cleaned for 5 scans prior to actual ablation.

To obtain time-integrated optical emission spectra of the ablated plasma, the plasma plume was imaged by using a focusing lens onto a quartz optical fiber connected to a spectrometer with 600 lines/mm grating, blazed at 400 nm (AvaSpec-3648 USB2). The spectral range was 183–753 nm with spectra resolution of 0.32 nm. The optical emission spectra of the plasma plume were integrated for 1 s, i.e. over 10 laser pulses and these were recorded at distances 0, 2 and 10 mm from the target surface.

For thin-film deposition, Si, MgO, GaAs substrates were placed at 45 mm from the target. Si or Ge films were deposited at room

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temperature for 18,000 pulses (10 Hz). The film thickness was measured using a white light interferometric microscope (Zygo) and a profilometer (Veeco Dektak Profiler), where a step was created by masking an area of the substrate. The deposited films were characterized by using Raman spectroscopy (Horiba HR800UV, 633 nm), scanning electron microscope (Zeiss Ultra and Supra, 1–5 kV) and a contact mode atomic force microscope (AFM, Digital Instr., Veeco Nanoscope) with a Si_3N_4 tip.

3. Results and discussions

3.1. Optical emission spectroscopy of plasma plume

The optical emission spectra for 355 nm, 532 nm and 1064 nm laser ablated plasma were obtained but the optical emission from 248 nm laser ablation was too weak to be detected for both Ge and Si. The maximum fluence used here was slightly below the reported ablation threshold for Si in vacuum at 193 nm [22]. The optical emission spectra for 1064 nm laser ablation of Si taken at 2 mm from the target surface at different laser fluence are shown in Fig. 1. The atomic lines of Si (SiI/Si, SiII/Si^{+}, SiIII/Si^{2+} and SiIV/Si^{3+}) with documented transition probabilities are included for identification [23]. A broad spectra centered around 350 nm can also be seen, only from the 1064 nm ablation when fluence increased. The intensities for SiI, SiII, SiIII and GeI and GeII [24] were extracted and plotted against laser fluence for 355 nm, 532 nm and 1064 nm in Fig. 2. The selected lines for detail comparison are shown in Table 1. SiIV lines were not included as the intensity was too low and the line overlapped with the emission lines from other species.

3.2. Si and Ge films

Si and Ge films were deposited for 1.5, 3 and 6 J/cm^2 using 355/532/1064 nm, and at 3 J/cm^2 by using the 248 nm laser. Spherical particles with diameters of 20 nm and up to 8 μm were detected on all the films. Large micron-sized round particles of (1–8) μm (referred to as 'droplets') were formed at high fluences. Typical droplets of Ge on GaAs are shown in Fig. 3. The droplet density was in the range of 10^4–10^5/cm^2, and was higher for Ge than Si. The fluence thresholds at which the large droplets were detected decreased from >6 J/cm^2, to 3 J/cm^2 and 1.5 J/cm^2 with longer laser wavelength for Ge. The fluence threshold for Si remained to be 3 J/cm^2

Smaller particles with mean size of 30–80 nm for Si and 60–120 nm for Ge (referred to as 'nanoparticles') were always observed on Si and Ge films for all laser wavelengths and fluence. The mean height was below 10 nm as obtained from AFM. Fig. 4 showed the Ge and Si nanoparticles deposited on a GaAs substrate. The density of the nanoparticles was in the range of 10^8/cm^2, 3–4 orders higher than the large micron sized droplets. With the excitation laser beam of the Raman Spectrometer of <2 μm, we were able to probe the Ge

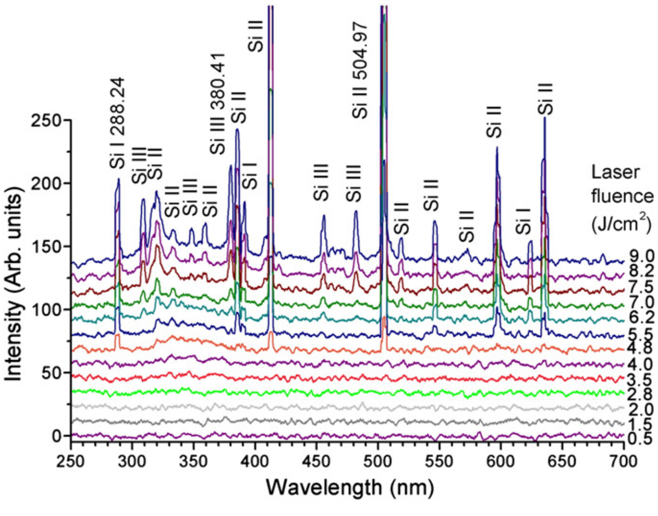

Fig. 1. Optical emission spectra of 1064 nm laser ablated Si plasma.

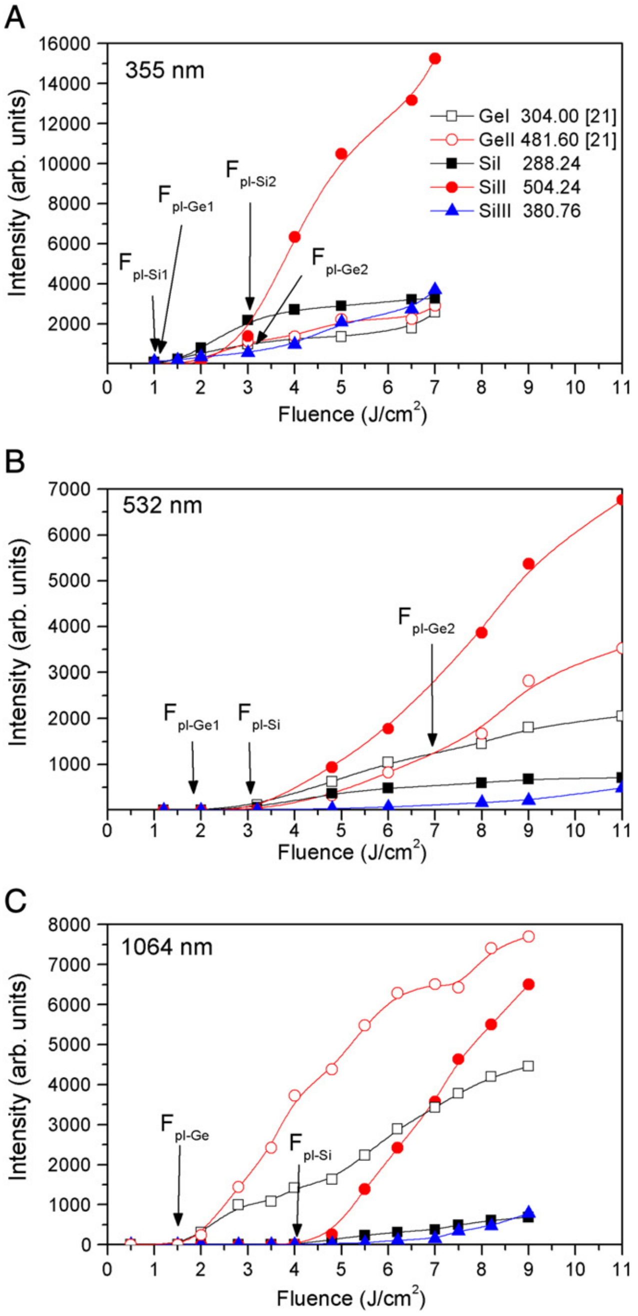

Fig. 2. The intensity of Si species and Ge [21] for (a) 355 nm, (b) 532 nm and (c) 1064 nm as a function of laser fluence.

Table 1
Si and Ge lines and the transition properties [20].

Ion	λ (nm)	Relative Intensity	Configurations	Terms
SiI/Si ^{0}	288.24	1000	$3s^23p^2$–$3s^23p4s$	^{1}D–^{1}P°
SiII/Si$^+$	504.24	1000	$3s^24p$–$3s^24d$	^{2}P°–^{2}D
SiIII/Si^{2+}	380.76	30	$3s4p$–$3s4d$	^{3}P°–^{3}D
GeI/Ge^0	304.00	750	–	–
GeII/Ge$^+$	481.60	1000	–	–