Optical and structural properties of Ge films from ion-assisted deposition

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ABSTRACT

The optical properties and microstructure of germanium (Ge) films, prepared by ion-assisted deposition (IAD) process, were investigated. The Ge films were deposited on sapphire and silicon substrates, with and without simultaneous Ar^+ bombardment. Higher index films, with a refractive index 7.7% larger than that of the single crystalline Ge wafer, were obtained with the IAD process. The density of the IAD film could be 1.5% greater than that of the e-beam film. The results of the heat treatment indicated that the optical and structural properties of the IAD films were more stable. Ge nano-crystallites could be observed under high ion power density, which induced a crystalline structure in the Ge thin films. The average size of the nano-crystallites, as determined from both the X-ray diffraction data and the transmission electron microscopy images, showed that no systematic change had occurred. The results presented in this work suggest that the optical and structural properties of Ge thin films can be effectively modified by the application of the IAD process.

1. Introduction

Germanium (Ge) is one of the most useful materials in the microelectronic and optical industries. Ge films are used in the optical and photonic industries for solar cells and photo-thermal applications [1–3]. Their high refractive index and broad transparent band also are widely used in the rapidly expanding area of infrared optical systems [2]. Over the past few decades, the optical and structural properties of Ge thin film whether prepared by electron beam evaporation process [4–10] or by other physical vapor deposition processes [11–13] have been extensively discussed. In recent years, there has been renewed interest in the application of ion-assisted deposition (IAD) techniques for the preparation of Ge thin film [14–16]. However, what seems to be lacking is research focused on the relationship between the optical and structural properties, and the parameters of the IAD process.

The purpose of the present work is to investigate the optical and structural properties of Ge thin films prepared by the IAD process, and to compare them with those of films grown by the conventional e-beam evaporation method. We determined the optical constant in the mid-IR range of Ge thin films grown by the IAD process via infrared variable angle spectroscopic ellipsometry (IR-VASE®). The spectral transmission of the annealed films was also obtained by Fourier transform infrared (FTIR) spectroscopy. The structural properties of these films were analyzed by white light interferometry, as well as by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A heat treatment was carried out and the influence of ion bombardment on the optical and structural properties of the Ge thin films was scrutinized.

2. Experiments

Ge films were deposited on B270 glass, sapphire and n-type silicon <100> substrates using a commercial thin film coater (Optorun Co., OTFC-1100 series) equipped with a 17 cm radio-frequency ion source (Optorun Co., OIS-One). The substrates were first cleaned by the standard procedure to remove surface contaminants, followed by 56 mW/cm² ion bombardment for 5 min, prior to deposition. The single crystalline Ge source material (which had a purity of 99.9999%) was evaporated by an electron beam gun. The deposition chamber was evacuated to a base pressure of 6.6×10^{-4} Pa by a cryo-pump. The working gas was argon, and the operating pressure was maintained at 2.6×10^{-2} Pa by an automatic pressure control unit during the IAD process. In order to monitor the effect of the ion-assisted technique on the optical and structural properties, the ion energy was varied from 100 eV to 600 eV, the current density was varied from 12 μA/cm² to 45 μA/cm², and the ion power density varied from 1.2 mW/cm² to 27 mW/cm². The current density was detected by a commercial measuring program (Optorun Co., OIS-CDMP X30). The thickness of the films was in the region from 270 to 310 nm. The optical constants did not depend on the thickness of the film [16]. The deposition rate was controlled at 0.6 nm/s by a quartz-crystal monitor (Inficon Co., IC/5), and the substrate was heated to 100 °C during deposition.

The stabilization of the optical and structural properties of the Ge thin film was determined after annealing some selected films in a

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vacuum infrared heating furnace which had been evacuated to 1.3×10^{-2} Pa by a turbo-pump prior to heating. The films were annealed at 150 °C, 250 °C, 350 °C, or 450 °C for 2 h, after which the spectral transmission and the crystalline structure of the resultant films were measured.

The optical constants of the Ge thin films were determined by an infrared variable angle spectroscopic ellipsometer (IR-VASE® made by J.A. Woollam Co.) at room temperature. The IR-VASE® instrument is a spectroscopic ellipsometer capable to cover a wide spectral range from 2 to 30 μm. The system used consisted of a commercially available infrared spectrometer source (BOMEM MB-102), a rotating polarizer, and a rotating compensator. The sample was mounted on a high precision stage, and the measuring process was controlled by a computer. The infrared transmission spectra of the Ge films deposited on the sapphire substrate were obtained by a FTIR spectrophotometer (BOMEM MB-100). The surface roughness and surface morphology were determined by a white light interferometer (WLI) (Zygo NewView 5032). The WLI system noise resulted from a number of factors, including electronic noise, sensor noise, and small vibrations caused by changes in the measurement environment. This system noise was about 0.07 nm, which was quantified as a function of measurement averages using a built-in process. SEM was done with a JEOL JSM-6700F operated at 10 kV. The resulting images show a cross-sectional view, and display the thickness of the films deposited on the silicon substrate. The crystalline structure of the films deposited on the B270 glass and sapphire substrates was investigated by XRD (carried out on a Bruker AXS D8) using CuKα radiation ($\lambda = 0.15406$ nm) operated in locked coupling mode. The scanning rate was 4°/min throughout. The size of the crystallites in the films was calculated from the full width at half maximum (FWHM) of the resultant diffraction peak. The results of TEM (JEOL JSM-2010F operated at an accelerating voltage of 200 kV) on some selected sample films were compared with the XRD measurements. Samples for TEM observation were deposited on a silicon substrate. The samples were first cut into two pieces which were then glued together with the film surfaces facing each other. After the preliminary grinding and pre-thinning procedures, the samples were bonded to a copper ring with a diameter of 3 mm. The specimen was thinned by ion milling to generate the electron transparent area.

3. Results and discussion

The refractive indices in the infrared wavelength range (2–14 μm) of Ge thin films deposited on a silicon substrate are shown in Fig. 1. The dotted line refers to the refractive index of the single crystalline, n-type, <111> orientation, Ge wafer with a thickness of 1 mm. The deviation
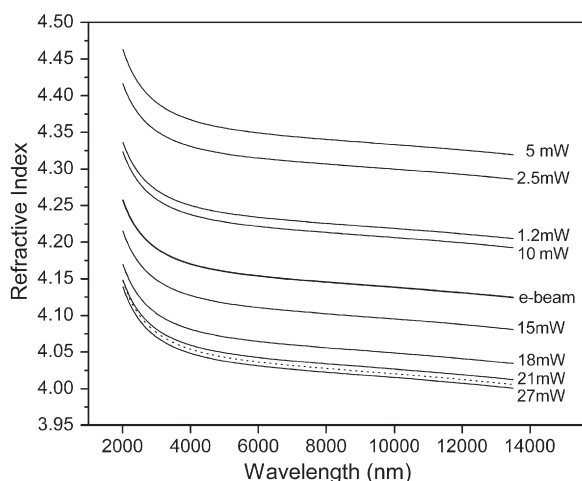
from the values given in the literature [17–19] is within 0.7%. It can be seen that the refractive index of Ge film is strongly dependent on the ion power density.

As can be observed in Fig. 1, the refractive index of the e-beam film was about 2.7% larger than of the bulk Ge wafer. This ratio is in good agreement with the value from the literature [4,6]. A comparison with the e-beam film shows two clear regions of the influence of the ion power density. In the first region, the index increased with increasing ion power density from 1.5 to 5 mW/cm². The highest refractive index obtained for the IAD film was about 4.8% larger than that of the e-beam film, and about 7.7% larger than of the bulk Ge wafer. The ratio of the refractive index of the IAD film, which was deposited at an ion power density of 5 mW/cm², to the refractive index of the bulk Ge was much greater than that given in the literature [4–6]. The higher index obtained in this region is presumably related to the greater density of the film, caused by the ion bombardment. This enhanced the adatom surface mobility and which acted to densify the growing film. The ratio of the density of the evaporated film to the density of the bulk plate in terms of their refractive indices can be calculated from the Lorentz–Lorentz law [10]. The results of this calculation show that the density of the IAD film was about 1.5% greater than that of the e-beam film.

In a second series, the ion power density varied from 10 to 27 mW/cm². The higher the ion power density, the lower the index obtained. This might be due to the lower packing density caused by the sputtering effects, i.e., the formation of voids, holes, micro-cracks, and the generation of a crystalline structure. This will be discussed in greater detail below.

There was an insignificant influence of the ion power density on the extinction coefficient of each film. This might be due to the fact that the photon energy in infrared region is larger than the standard bandgap of Ge. However, the film thickness appears to be too thin to allow the detection of the infrared absorptions.

The surface morphology of the e-beam and IAD films was determined with a WLI. The surface roughness was represented as a root mean squared (rms) value. The results showed that the surface roughness of the Ge film decreased from 1.53 nm to 0.39 nm after the application of the IAD process. The e-beam film also showed some surface digs and a curved surface due to tensile stress, as shown in Fig. 2(a). In contrast, there were no obvious digs or bending of the surface observed in the IAD films, as can be seen in Fig. 2(b). These smooth planar surfaces were obtained because of destroying surface clusters during the ion bombardment. When the ion power density was less than 2.5 mW/cm², the surface of the film remained curved, but the surface roughness decreased as the ion power density increased. Once the ion power density exceeded 2.5 mW/cm², we begin to observe a planar surface. The change in the surface curvature indicates that the stress in the Ge film had indeed been modified by the IAD process. When the ion power density was greater than 2.5 mW/cm² but smaller than 15 mW/cm², there was no significant difference in surface roughness between these films. The surface roughness of the films increased when the ion power density gradually rose to 18, 21, and 27 mW/cm², which were the three highest ion power densities used. However, the surface roughness was still lower when the film was deposited at an ion power density less than 2.5 mW/cm².

All films were inspected by SEM. As shown in Fig. 3, there was no obvious cracking, voids or other defects inside either the e-beam or inside the IAD films, when deposited with a power density not in excess of 10 mW/cm². On the other hand, voids formed in the microstructure when the ion power density was greater than 10 mW/cm². As the ion power density increased, the defects became more severe, which resulted in a decrease in the refractive index. Several factors could have caused these defects. First, the injection of high energy Ar⁺ ions into the film led to a displacement of the Ge atoms. Second, the higher ion power not only simultaneously enhanced the sputtering effect, but also increased the possibility of argon being trapped within the film during the film growth. Both effects would lead to void structures.

Fig. 1. Refractive index vs. wavelength for different ion power densities.