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Growth of high-Sn content (28%) GeSn alloy films by sputtering epitaxy

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ABSTRACT

Crystalline GeSn thin films with Sn content up to 0.28 were deposited on Sn graded GeSn buffer on a Ge substrate at low temperatures by sputtering epitaxy. The structural properties of the high-Sn content GeSn alloy films were characterized by high resolution transmission electron microscopy and X-ray diffraction. The effect of annealing on the segregation of Sn in the high-Sn content GeSn film was investigated, and both the $Ge_{0.72}Sn_{0.28}$ and the $Ge_{0.8}Sn_{0.2}$ films were found to be stable after annealing at temperatures below 400 °C, which meets the needs of thermal budget for future photonic devices fabrication. The present results indicate that sputtering epitaxy is cost-effective method for growing high-Sn GeSn films.

1. Introduction

As complementary metal oxide semiconductor (CMOS)-compatible group IV materials, germanium tin (GeSn) alloys have potential applications in both photonics [1–9] and microelectronics [10–12]. Although Ge is an indirect bandgap semiconductor, GeSn alloys can become a direct bandgap semiconductor when the Sn content exceeds 7% [13], which is very promising for the fabrication of efficient Si-based lasers. Recently, the fabrication of optically pumped GeSn lasers operated in either microdisk or Fabry–Perot mode has been reported, providing the great opportunity for realization of optoelectronic integrated circuits (OEIC) [6–9].

In theory, the bandgap of GeSn alloys can be decreased from 0.66 (pure Ge) to 0 eV (α-Sn) by increasing the Sn content in the matrix. With an increase in the Sn content, the energy difference between Γ and L valleys increases, and this further improves the efficiency of GeSn-based light sources in terms of lasering threshold and operating temperature [6,9]. Detectors operating in mid- and far-infrared regions are usually made of III–V or II–VI group materials, which are not compatible with CMOS techniques. Thus, the narrow bandgap property of high-Sn content GeSn alloys is applicable for fully integrated Si photonic systems used in mid- and far-infrared applications.

In recent years, many deposition techniques such as molecular beam epitaxy (MBE) [1,4,5], chemical vapor deposition (CVD) [2,6,8,9], and sputtering epitaxy [14,15] have been developed for the epitaxial growth of GeSn. However, the following major obstacles have to be overcome for the epitaxial growth of high Sn content GeSn alloy films: larger lattice mismatch between Ge and GeSn and lower epitaxy temperature to avoid segregation of Sn at the surface. Up to now, GeSn alloy films have been prepared with Sn content of approximately 25% by MBE at 120 °C [16]. Moreover, polycrystalline GeSn with 25% Sn content has also been prepared by Sn-induced crystallization of amorphous Ge at 70 °C [17]. However, it is time-consuming and difficult to deposit GeSn films with high uniformity using this technique. The atom energy obtained by sputtering is much larger than that by MBE or CVD. Therefore, sputtering epitaxy is a promising method to deposit high-Sn content GeSn alloy films at ultra-low temperatures.

In this paper, we report the growth of GeSn crystalline films on graded Sn content buffers at ultra-low temperatures by sputtering epitaxy. The GeSn alloy films were deposited with Sn contents up to 0.28. The effects of thermal annealing on the structural properties and Sn segregation of the high-Sn content GeSn alloy films were investigated in detail to explore the applicability of these alloys for the fabrication of future devices.

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The $Ge_{1-x}Sn_x$ alloy films were deposited on 4-in. Ge(1 0 0) substrates by co-sputtering Ge and Sn targets arranged in a sputter-up configuration for confocal thin film deposition [14,15]. Before inserting into the chamber, the native oxide layer on the Ge substrate is removed in diluted HF solution. The base pressure of the sputtering chamber is less than 2×10^{-7} Torr. During the deposition, the sputtering pressure is kept at 3 mTorr in high pure Ar ambient. Prior to the growth of high-Sn content GeSn alloy films, a graded GeSn buffer layer comprising 100 nm-thick $Ge_{0.95}Sn_{0.05}$ and 30 nm-thick $Ge_{0.9}Sn_{0.1}$ films were deposited on the Ge(1 0 0) substrate. Subsequently, 20 nm-thick GeSn films with Sn contents of approximately 0.2 and 0.28 were deposited. The substrate temperature was varied between 100 and 160 °C depending on the Sn content. The variation of the Ge and Sn composition in the GeSn films was achieved by maintaining a constant RF power of 70 W for the Ge target and varying the Sn target from 9 W to 30 W. The deposition rate of Ge is about 1.7 Å/s, and the deposition rate of Sn is between 0.03 and 0.7 Å/s. After the deposition, the samples were cut and annealed at temperatures between 250 and 450 °C for 30 s by rapid thermal annealing (RTA). High resolution X-ray diffraction (HR-XRD) ω-2θ scans were used to investigate the crystalline quality of the $Ge_{1-x}Sn_x$ layers prepared at various Sn contents. High resolution cross-sectional transmission electron microscopy (HRTEM) was conducted to investigate the structural properties of the film on the atomic scale. Raman scattering experiments were performed at room temperature in the backscattering configuration using a Jobin–Yvon HR 800 Raman spectrometer, and the 488 nm line of an Ar^+ laser was used at normal incidence for excitation. Atomic force microscopy (AFM) was used to analyze the surface morphology after the RTA treatments.

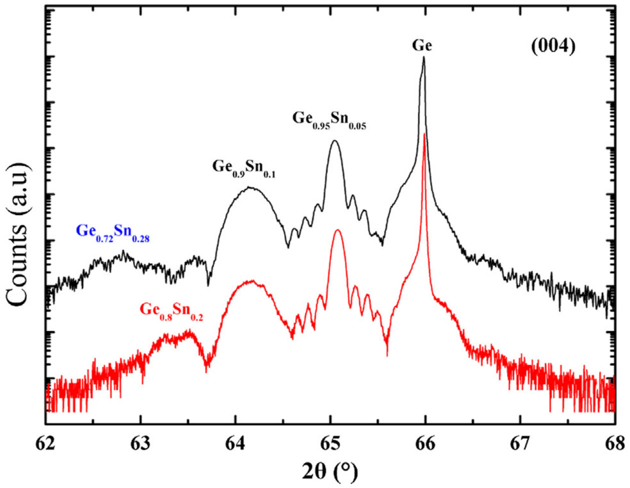

Fig. 1. HR-XRD (0 0 4) ω-2θ scans of the $Ge_{0.72}Sn_{0.28}$ and the $Ge_{0.8}Sn_{0.2}$ samples.

2. Results and discussion

Fig. 1 shows the XRD patterns of the $Ge_{1-x}Sn_x$films deposited on buffered GeSn layers. The XRD peaks of the GeSn film and the Ge substrate are distinct in Fig. 1. From the (0 0 4) and the (2 2 4) HR-XRD scans, the in-plane lattice constants ($a_{//}$) of the $Ge_{0.95}Sn_{0.05}$ and the $Ge_{0.9}Sn_{0.1}$ buffer layers were found to be nearly the same, approximately 0.5658 nm, while the calculated perpendicular lattice constants ($a_\perp$) were approximately0.5731 and 0.5801 nm, respectively. This indicates that the GeSn graded buffers are fully strained. The XRD peak positions of the $Ge_{0.8}Sn_{0.2}$ and the $Ge_{0.72}Sn_{0.28}$ films shift toward smaller 2θ values with increase in the Sn content. The perpendicular lattice constants ($a_\perp$) of the $Ge_{0.8}Sn_{0.2}$ and the $Ge_{0.72}Sn_{0.28}$ films were calculated to be 0.5866 nm and 0.5911 nm, respectively and are in agreement with those obtained from HRTEM analyses, as discussed below. According to Wang et al., the critical thickness of$Ge_{0.8}Sn_{0.2}$ film deposited on Ge is only several nanometers [18]. This suggests that the top GeSn layer is likely relaxed. Using Vegard's law, the relaxed lattice constants (a_0) of $Ge_{0.8}Sn_{0.2}$ and $Ge_{0.72}Sn_{0.28}$ were found to be 0.5824 nm and 0.5890 nm, respectively [19]. The nearly comparable values of $a_\perp$ and a_0 confirm the relaxation of the top GeSn layer.

Figs. 2 and 3 show the HRTEM images of the $Ge_{0.8}Sn_{0.2}$ and the $Ge_{0.72}Sn_{0.28}$ films. The GeSn graded buffer is almost defect-free with a high crystalline quality. This is because the GeSn buffer layer is deposited pseudomorphically (fully strained) on the Ge substrate, as revealed by the HR-XRD results. It is clear from the HRTEM images that both the top high-Sn content GeSn layers are crystalline even though they were deposited at a low temperature. However, the top GeSn layer exhibits threading defects and vacancies due to the strain relaxation process. To further investigate the structural properties, the fast Fourier transform (FFT) patterns of the $Ge_{0.72}Sn_{0.28}/Ge_{0.9}Sn_{0.1}$ and the $Ge_{0.9}Sn_{0.1}/Ge_{0.95}Sn_{0.05}$ interface regions were recorded, and the results are shown in Fig. 3(d–f). The FFT images show typical diffraction patterns of diamond structure. The spots belonging to d_{002}, d_{220}, and d_{111} are indicated in the

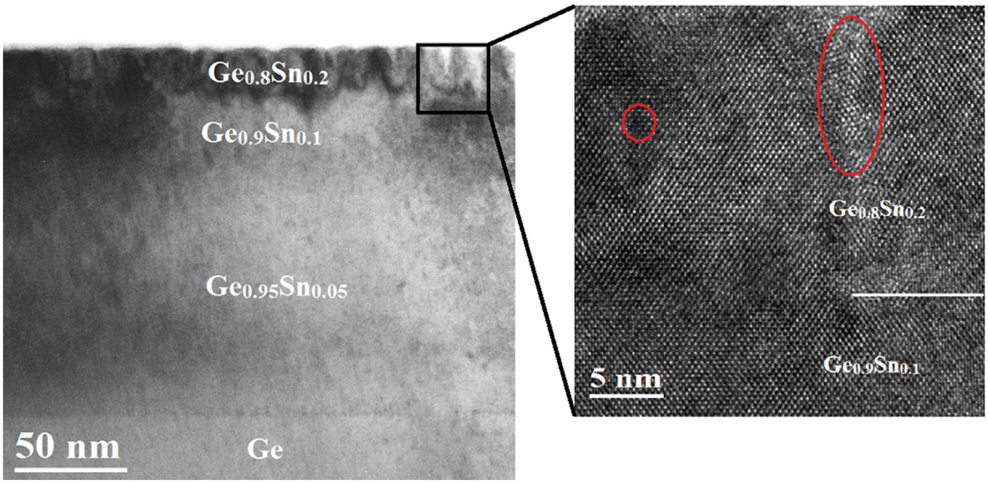

Fig. 2. HRTEM images of the $Ge_{0.8}Sn_{0.2}$ film deposited on the Ge substrate. The inset shows the interface region between $Ge_{0.8}Sn_{0.2}$ and $Ge_{0.9}Sn_{0.1}$. The red circles indicate threading defect and vacancy.