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Structural and optical studies of strain relaxation in $Ge_{1-x}Sn_x$ layers grown on Ge/Si(001) by molecular beam epitaxy

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ABSTRACT

The structural and optical properties of the $Ge_{1-x}Sn_x$ layers with Sn mole fraction x of about 0.04 and 0.07 grown by molecular beam epitaxy on strain relaxed (001) Ge buffer layers have been investigated. The formation of GeSn solid solutions is proved by the high-resolution X-ray diffraction and micro-Raman investigations. The $Ge_{1-x}Sn_x$ layers are found to be partially relaxed, the degree of strain relaxation increases from 8% in the layer with $x = 0.04$ to about 14% in the layer with $x = 0.07$. For the Ge and $Ge_{1-x}Sn_x$ layers the miscut and tilt angles were calculated and compared with those predicted by Nagai's theory. For the $Ge_{1-x}Sn_x$ layer with $x = 0.07$ an abnormally large tilt of about 0.26° of the epilayer (001) lattice planes with respect to the corresponding substrate planes is found. It is shown also that the epilayer tilt axis is rotated on about 90° with respect to the direction of a substrate miscut. The possible mechanisms of the effect are discussed.

1. Introduction

The interest in the research and development of Sn-containing semiconductors based on group IV elements, in particular of GeSn alloys, is motivated by promising prospects for their usage in optoelectronic and microelectronic devices on Si platform [1]. Nowadays, Ge plays an important role in advanced optoelectronics because of its high carrier mobility and optical absorption at telecommunication wavelengths, as well as of its compatibility with existing Si processing and lattice matching with III-V semiconductors of different band gaps [2]. However, Ge is an indirect band gap semiconductor that prevents its application in light-emitting devices. The incorporation of Sn in Ge matrix offers exciting possibilities for engineering of band structure and carrier mobility in the GeSn alloy system [1].

Firstly, the systematic increase of Sn content in the GeSn alloy reduces the Γ-L valley separation and lowers the direct band gap. Theoretical calculations predict for GeSn the transition from an indirect to a direct semiconductor at around a 6–10% of Sn content in the unstrained material [3,4]. The room-temperature photoluminescence originated from direct band gap transitions in the GeSn layers [5,6] as well as the electroluminescence from diode structures with active GeSn layers [7–10] have been observed.

The reduction of the energy gap in the GeSn alloy leads also to a substantial improvement in the absorption properties in the infrared wavelength range up to 1800 nm. It has been shown that Sn concentrations as small as 2% are sufficient to achieve absorption coefficients that cover the whole telecommunication windows and are at least 10-fold higher as compared with Ge in C- and L-bands [11]. The GeSn p–i–n photodetectors fabricated by standard processes fully compatible with conventional Si complementary metal-oxide semiconductor technology are found to be highly attractive for applications in both optical communications and optical interconnects [12–14].

GeSn alloys are predicted also to have an increased electron and hole mobility by a factor of 4 as compared with Ge [15] which makes it promising to use as a channel material in metal oxide semiconductor field effect transistors (MOSFETs). In fact, GeSn pMOSFETs with channel Sn composition of 7% showed enhancement in hole mobility over control Ge devices by 85% [16].

The unstrained buffer layers of GeSn can be used also as uniaxial compressive stressors for Ge channels in high performance Ge-MOSFETs and tunnel-field effect transistors [17,18] owing to larger lattice parameter of GeSn as compared with Ge. The advantages of uniaxially strained Ge channels are: higher drift current, high hole mobility and smaller shift of threshold voltage compared to the biaxially strained ones.

Thereby, both fully strained and strain relaxed GeSn layers of different Sn content are of interest for application in modern optoelectronic and microelectronic devices. However, epitaxial growth of GeSn alloys faces the challenges of large lattice mismatch between Ge and α-Sn (~14.7%), low solubility of Sn in the Ge matrix (~1%) and Sn surface segregation at growth temperatures higher than 140 °C [19]. To inhibit Sn

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segregation in GeSn alloy the low growth temperatures are required though the low temperature growth results in the surface roughening and limited critical epitaxial thicknesses [20]. It has been demonstrated that metastable GeSn films with Sn content up to 26% and no signs of Sn segregation can be grown epitaxially on Ge substrate at temperatures lower than 100 °C [20]. The understanding of the mechanisms of strain relaxation in the GeSn/Ge heterostructures is of particular importance for their advantageous use in modern devices.

This study presents the results of structural and optical investigations of $Ge_{1-x}Sn_x$ films with x of about 0.04 and 0.07 grown on relaxed Ge layers by molecular beam epitaxy (MBE).

2. Experimental details

The Ge and GeSn layers were grown by MBE in a Katun MBE system. Growth mode was controlled in situ by reflection high energy electron diffraction (RHEED).

Ge buffer layers of 1.5 μm thickness were grown on (001) Si substrates at a temperature of 650 °C. A two domain reconstruction of type $(2 \times 1) + (1 \times 2)$, which is typical for the (001) orientation, was observed in the RHEED patterns for the surface of the Ge buffer layers.

The GeSn layers of about 0.4 μm thickness and Sn content of about 4% or 7% were grown on Ge buffer layers at a temperature of 150 °C and a deposition rate of 8 nm/min. The observed RHEED patterns indicate that the epitaxy of the GeSn layers proceeds with the same type of surface reconstruction as the Ge buffer layers at 650 °C, but is accompanied with the formation of facets on the surface of GeSn layer. The surface roughness of the films was studied by atomic force microscopy. A root-mean-square roughness was found to be about 1 nm for the Ge buffer layer and in the range of 4–6 nm for the GeSn layers.

Three types of heterostructures were investigated: (i) 1.5 μm Ge buffer layer grown on Si substrate; (ii) 0.4 μm $Ge_{0.96}Sn_{0.04}$ layer grown on 1.5 μm Ge buffer layer/Si substrate; and (iii) 0.4 μm $Ge_{0.93}Sn_{0.07}$ layer grown on 1.5 μm Ge buffer layer/Si substrate.

The structural properties of the samples were studied by the high-resolution X-ray diffraction (HRXRD) and secondary neutral mass spectrometry (SNMS) methods. The HRXRD measurements were carried out using a high resolution X-ray diffractometer X'Pert PRO MRD with a $4 \times$ Ge (220) monochromator and Cu anode. The SNMS measurements were performed in the high frequency (HF) mode of the sample sputtering by Ar^+ ions with energy 300 eV in INA-3 (Laybold-Heraeus, Germany) instrument. These ions were generated due to the application of HF voltage in the form of rectangular negative pulses between sample and wall of the low pressure (3.26×10^{-2} mbar) argon radiofrequency (27.12 MHz) plasma. The voltage frequency was 100 kHz (50% duty cycle). The area of sputtering was limited by the tantalum diaphragm with the internal diameter 3 mm. The sputtering rate was approximately 0.5 nm/s. The depth scale was determined for each profile by measuring the crater depth with a Dektak 3030 profilometer.

The micro-Raman study was done using a triple Raman spectrometer T-64,000 Horiba Jobin-Yvon with an excitation by a 647.0 nm line of an Ar–Kr ion laser at room temperature in the backscattering from (100) plane in parallel $z(x,x)\bar{z}$and crossed $z(x,y)\bar{z}$-geometries, where x, y and z correspond to {100}, {010} and {001} directions of the cubic crystal structure, correspondingly.

3. Results and discussion

3.1. SNMS investigations

Fig. 1 shows the SNMS profiles for Sn and Ge distribution in the depth of GeSn films. The SNMS investigations reveal the Sn content in the ranges of 3.5–4% and 7.5–8.3% for two GeSn films studied. The distribution of Sn is found to be rather uniform excepting for a lower Sn content at the beginning of the growth, i.e. in the first 30–50 nm of the GeSn films. A formation of compositionally graded layer with reduced Sn content near the GeSn/Ge interface has been reported for the GeSn films grown on Ge by MBE [21] or chemical vapor deposition (CVD) [22]. This was explained by the growth mechanism including rate-limiting incorporation of Sn from a surface adlayer [21].

In fact, the Sn depth profile in the GeSn layer with 7% of Sn shows an increased Sn content (up to about 16%) near the film surface. A thickness of this Sn-enriched region is of about 1.5–2 nm that is smaller than depth resolution of the SNMS method of ~4 nm. Therefore, we cannot distinguish between thin Sn-rich near surface region caused by Sn precipitation and the increased Sn signal caused by the presence of residual impurities, oxide or other contaminations on the film surface. As a rule, Sn precipitation occurs during the growth or upon the post-deposition thermal treatment in the two ways: (i) formation of Sn-rich nanoparticles at around the surface of the film or within the layer, and (ii) formation of thin Sn-enriched layer near the film surface. The reported sizes of Sn inhomogeneities vary from tens to several hundred nanometers [20,23–25]. The SNMS investigations do not reveal large depth inhomogeneities of Sn distribution in the GeSn films studied. However, it cannot exclude the presence of small Sn-rich precipitates owing to low spatial resolution in lateral direction of the SNMS method.

3.2. Raman spectra investigations

The Raman spectra of the structures studied (Fig. 2) show a strong Ge LO phonon peak in the range of 297–302 cm^{-1}. Besides the Ge–Ge phonon mode, the Raman spectra of the GeSn films exhibit a clear Sn–Sn vibration mode in the range of 180–186 cm^{-1} and a Ge–Sn mode in the range of 259–264 cm^{-1}. These modes are not observed in pure Ge buffer layer and are the evidence of GeSn solid solution formation.

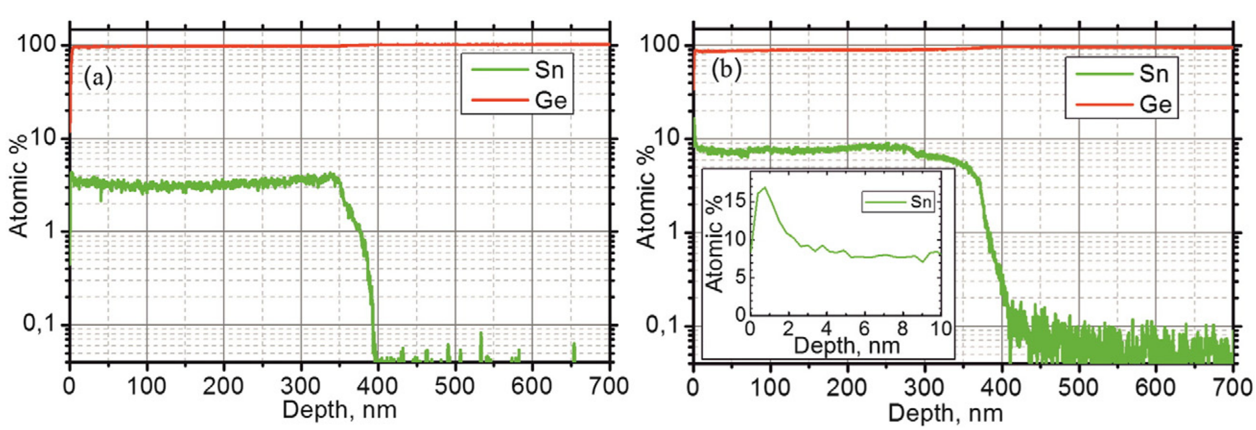

Fig. 1. SNMS depth profiles of Sn and Ge distribution in the structures with Sn content of about 4% (a) and 7% (b).