Atom probe tomography study on $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ hetero-epitaxial film on Ge substrates

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We analyzed the incorporation of C atoms into a ternary alloy $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ epitaxial film on Ge substrates on a sub-nanometer scale by using atom probe tomography. Periodic atom distributions from individual (111) atomic planes were observed both in the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and at the Ge substrates. Sn/C atoms had non-uniform distributions in the film. They also demonstrated a clear positive correlation in their distributions. Substitutional C atoms were only incorporated into the film when an Sn atom beam was applied onto the substrates under film growth conditions.

1. Introduction

Group IV semiconductor ternary alloys have the potential for energy bandgap engineering with independent lattice constant tuning and multilayer structures [1]. Hence, their application to multijunction solar cells has been expected and investigated [2,3]. The incorporation of substitutional C atoms is the key to achieving the required top layer with a wider bandgap in multijunctions composed of Group IV alloys. However, there has been difficulty in preparing a higher C content in Ge based layers because C atoms easily transfer from substitutional to interstitial sites to precipitate in $\text{Ge}_{1-x}\text{C}_x$ binary alloys due to their very low thermal equilibrium solid solubility of 10^8 cm^{-3} into Ge layers [4,5]. A solution has been predicted in which C atoms in $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ should be more energetically stable at substitutional sites by incorporating Sn atoms and taking into consideration bond energy and compensation for distortion [6]. However, the atomic scale structure of Sn and C in $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ ternary alloys has not yet been experimentally understood in detail. We examined the incorporation of C atoms into epitaxial $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film on Ge substrates in this study by using atom probe tomography (APT) to uncover the effects of Sn on C behavior.

APT is a powerful tool to demonstrate the 3D mapping of atoms in crystal on a sub-nanometer scale. Laser-assisted (La-) APT [7-10] has recently been applied to avoid clustering during the evaporation of atoms at the edges of needle-shaped probes to improve the resolution of atom positions. The spatial resolution of atom probes parallel to that of needle-shaped probes, which will be called depth resolution after this, was proven to be much higher than that obtained with secondary ion mass spectrometry [11, 12]. La-APT actually provided a higher resolution than that from the periodic atom distribution that arose from individual (111) atomic planes in diamond structure crystals like Si [13]. Only $\text{Ge}_{1-x}\text{Sn}_x$ film had previously been analyzed by APT and reported [14] for Ge based group IV semiconductor alloys.

The present paper is the first to report the 3D mapping of $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film by using APT, at least to the best of our knowledge.

2. Experimental details

How the samples were prepared will be briefly described in what follows. Ge (001) bulk wafers were thermally cleaned by annealing them at 490 °C in an ultra-high vacuum (UHV) chamber after they had been chemically cleaned before the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film was grown. After cleaning, $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ layers were heteroepitaxially grown on the cleaned surface of a Ge wafer in a radio frequency (RF) magnetron sputtering system with Ar plasma and individual pure Ge, Sn, and C targets in the same UHV chamber. The substrate temperature during growth was controlled at ~450°C, and the target thickness of these layers was 160 nm. Target content, based on the deposition rate of each metal, was set at $x=5\%$ and $y=7\%$ but the actual content in the sample was $x=6\%$ and $y=5\%$ determined by using X-ray photoemission spectroscopy (XPS). No C or Sn precipitation was detected by conventional secondary electron microscopy on the surface of $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$. However, C based precipitation was observed on the surface of the $\text{Ge}_{1-x}\text{C}_x$ binary alloy film deposited under the same conditions as $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film except for the supply of additional Sn atoms. The incorporation of C atoms into the deposited $\text{Ge}_{1-x}\text{C}_x$ film was actually also not observed in the following analysis with APT. This fact simply indicated that the addition of Sn made it easier to incorporate C atoms into the growing film.

The needle-shaped probes for APT were prepared with a focused ion beam technique using the Helios 450 model produced by FEI Corp. The probes had an orientation parallel to the (111) crystal direction of $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ or the Ge substrate. La-APT was carried out with AMETEK's LEAP 4000Xsi model. The laser pulse mode was selected with a wave-length of 355

nm. The specimen temperature and the intensity of the laser pulse during APT analysis were at 30 K and 20 pJ for the previously mentioned $\text{Ge}_{1-x}\text{C}_x$ film, and 20 K and 20 pJ for the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film. These conditions were selected by optimizing the balance that conflicted between obtaining a higher resolution for the reconstructed atom positions and fracturing the probes, due to the higher evaporation field of C atoms than that of other compositional atoms in the film.

3. Results

The mappings for Sn atoms in Figs. 1(d)-(f) and for C atoms in Figs. 1(g)-(i) were obtained with the probes by dividing the atomic structure into three sliced planes (Slices A–C) having thicknesses of 2 nm, as shown in Fig. 1(a). Figures 1(b) and 1(c) show the total amount of Sn/C atoms in the three sliced planes. The Sn/C atoms featured non-uniform distributions throughout the whole film. Their distributions were also correlated. The arrows on the dotted lines in Figs. 1(d) and 1(g) are parallel to the (111) plane, which also indicate non-uniform distributions in the Sn/C atoms. These directions tended to spread dislocations in diamond structured crystals, whose existence in other portions of the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film had been confirmed by transmission electron microscopy [15]; therefore, Sn/C atoms could be collected through those dislocations.

Periodic atom distributions resulting from individual {111} atomic planes can be seen in both the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film with lower Sn/C concentrations and the Ge substrate on a nanometer scale by tuning the viewing direction, as shown in Fig. 2. Their periodicities of 0.33 nm in the spatial distribution maps (SDMs) of Figs. 2(c) and 2(d) are the same. This means that the strain of the film is nearly fully relaxed, which was confirmed by the Raman shift in the phonon mode

in Ge-Ge bonds (not shown). The peak-valley ratio of SDM in $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film (Fig. 2(c)) was lower than that in the Ge substrate (Fig. 2 (d)). This was probably due to non-uniformity in atom distributions.

Figures 3(a) and 3(b) indicate the sub-nanometer scale distributions of Sn/C/Ge atoms of $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film in the lower and higher concentration portions in Fig. 2(a). Almost all Sn/C atoms are on the periodic atom distributions in the [111] direction. This was actually confirmed by comparing the SDM of Ge-Ge with that of Ge-C or Ge-Sn shown in Fig. 4. The clear coincidence of the peaks at distance=0 means that C or Sn atoms are in the same layer of the Ge atoms in this direction. Some Sn/C atoms in the higher concentration regions in Fig. 3, however, are not in the periodic atom distributions. It should be noted that C atoms are not always near Sn atoms although some of them seem to be near Sn atoms. These results seem to contradict the simple idea that the incorporation of C atoms at the nearest neighbors of Sn atoms are due to strain compensation by taking uniform strains into consideration. An Sn atom and a C atom in a Ge crystal, however, actually have atomistic interaction depending on the direction of bonding between atoms in a crystalline structure, as will be discussed in the next section. The concentrations of Sn/C atoms can be estimated by counting all atoms (Sn/C/Ge) in boxes like those in Fig. 3(a) or 3(b). The relation between Sn/C concentrations in each of the ten boxes with lower and higher concentrations is shown in Fig. 5. There is a clear positive correlation except for the open squares.

4. Discussion

The formation energy of substitutional C atoms in Ge crystal is so high (2.37 eV [3]) that the thermal equilibrium concentration of C atoms in Ge crystal is very low. Substitutional C

atoms were only incorporated into the film when an Sn atom beam was applied onto the substrate under the ternary alloy film growth conditions described in the present paper, as was previously explained. The correlation of Sn/C atom concentrations in Fig. 5 also reveals that Sn atoms and C atoms interact in the growing film. This does not, however, mean one-by-one correspondences which may mean individual interactions between Sn and C atoms in the neighborhood in Ge crystals, forming an individual binding state [6]. Conversely, the longer range atomistic interaction of Sn and C atoms in the same “zigzag Ge chain at not only the 1st neighbor but also the 2nd, 5th, and 8th neighbors had been expected that had binding energies in the range of 0.8–3.5 eV (further sites in the zigzag chain should also be energetically stable although no such calculations were done), while C atoms outside the zigzag Ge chain including Sn atoms have repulsive interactions [3]. This can explain why the film becomes stable when Sn and C atoms coexist at nearest neighbors in some cases but stays at a distance in many other cases during growth. In other words, C atoms can be stable and allowed to remain during growth not only at the nearest neighboring sites of Sn atoms, which have fewer possibilities of supplying C atoms due to the limited number of such sites, but also at many other sites of C atoms that are far from Sn atoms along the same zigzag chains. This must be the mechanism responsible for the incorporations of C atoms into the lower concentration portions of epitaxial $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film when additional Sn atoms are supplied onto Ge substrates. $\text{Ge}_{1-x}\text{C}_x$ films have tended to contain interstitial C atoms and/or their complexes in the literature [4]. However, this did not occur in our samples, and C atoms merely formed precipitates at the film surface. This difference might be caused by the method of growth and/or differences in their growth conditions.

There are two possibilities to explain the outliers (open squares) for the correlation between C and Sn atom concentrations in Fig. 5. The first is missing Sn atoms during the detection due to the higher concentration of C atoms. The surface migration of C atoms on the

atomic plane prior to evaporation might not have enabled Sn atoms to be detected due to the higher evaporation field of C atoms [16]. The second possibility is the actual increase in the incorporation of C atoms during film growth due to dislocations, which might exist in higher C/Sn concentrations areas. This may have caused additional C atoms not to have been detected beyond the nominal concentrations in Fig. 5, similarly to B atoms in highly B- doped silicon [17].

4. Conclusions

$\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ layers were heteroepitaxially grown on the cleaned surface of a Ge (001) wafer in a sputtering system with Ar plasma and pure Ge, C, and Sn targets. The incorporation of C atoms into epitaxial $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film at the Ge substrate was also analyzed with La-APT. Periodic atom distributions that resulted from individual (111) atomic planes could be observed both in the $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and at the Ge substrate. Sn/C atoms had non-uniform distributions in the film and demonstrated clear positive correlations in their distributions. The incorporation of substitutional C atoms only occurred when Sn atoms were simultaneously incorporated into the substrate under the film growth conditions presented in the present paper. C atoms can be stable and allowed to remain during growth not only at the nearest neighboring sites of Sn atoms, which have fewer possibilities of supplying C atoms due to the limited number of such sites, but also at many other sites of C atoms that are far from Sn atoms along the same zigzag chains.

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Figure Captions

Fig. 1. (a) Divisions of probe into three sliced planes (Slices A–C). (d), (e), and (f). Mapping of Sn atoms, and (g), (h), and (i) mapping of C atoms of slices A, B, and C having thicknesses of 2 nm. Total (b) Sn or (c) C atoms on these three sliced planes. Arrows on dotted lines in (d) and (g) are parallel to (111) plane coinciding with non-uniform distributions of Sn/C atoms.

Fig. 2. (a) Atom distributions in whole portion of both $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and (b) at Ge substrate. Periodic atom distributions on nanometer scale resulting from individual (111) atomic planes in both $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and Ge substrate. (c) Atom distributions in $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and (d) that at Ge substrate in [111] direction. Please ignore wheel-like symbol in (a), which appeared in graphical viewer for APT and could not removed.

Fig. 3. Atom distributions in whole portion in both $\text{Ge}_{1-x-y}\text{Sn}_x\text{C}_y$ film and at Ge substrate. (a) Atom distributions in lower and (b) in higher concentration portions on sub-nanometer scale.

Fig. 4. Comparisons of spatial distribution maps (SDMs). (a) between Ge-Ge and Ge-C and (b) between Ge-Ge and Ge-Sn.

Fig. 5. Relation between Sn/C concentrations in each of ten boxes for lower and higher concentrations of film. Open squares indicate boxes in which Sn atoms were missed during counting due to higher concentrations and evaporation field of C atoms.

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