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Epitaxial Growth of Germanium Thin Films on Crystal Silicon Substrates by Solid Phase Crystallization

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Abstract

We have investigated the solid phase crystallization (SPC) of amorphous germanium (a-Ge) precursors on single crystalline silicon (c-Si) substrates as seed layers. We successfully obtained the epitaxial-like growth by sufficiently reducing the impurity incorporation in the a-Ge precursors. The preferential growth following the substrate orientations depends on the characteristics of c-Si substrates. The n-type c-Si substrate with (100) orientation is the most suitable for the epitaxial-like growth, because the growth velocity is faster than that on the other substrates.

1. Introduction

Thin film solar technologies enable us to form stacking structures of multi-junction solar cells for higher energy conversion efficiency due to more utilization of the sunlight [1, 2]. We try to develop narrow band gap materials for bottom cells of multi-junction solar cells to utilize infrared light. We proposed to use crystalline germanium (c-Ge) films as the narrow band gap materials. The c-Ge has a sufficiently narrow gap which has sensitivity for infrared light of longer wavelength than1500nm [3-5]. However, c-Ge films grown by plasma-enhanced chemical vapor deposition (PE-CVD) or sputtering methods have micro-crystalline structures with random crystalline orientations [3-8]. The micro-crystalline Ge films have many grain boundary defects which strongly trap electrons, so they do not have sufficient quality for photovoltaic purposes [7-9].

We have investigated the solid phase crystallization (SPC) of amorphous (a-Ge) on single crystalline Si (c-Si) substrates [10-12]. We found that a-Ge easily incorporates impurities from air-exposed surface after the deposition of a-Ge and such impurities disturb the epitaxial-like growth following the c-Si substrates. We successfully obtained the epitaxial-like growth following the c-Si substrates by suppressing the impurity incorporation from the air-exposed surface to the a-Ge precursors [10]. On the other hand, the conductive type and crystal orientation of c-Si substrates affect the epitaxial-like growth. The c-Si substrates with n-type and (100) orientation are preferable to the preferential growth, but those with p-type or (111) orientation sometimes cause the random nucleation [11, 12]. In this report, we investigated the influence of c-Si substrates on the epitaxial-like growth of Ge and discussed the crystal growth on different c-Si substrates.

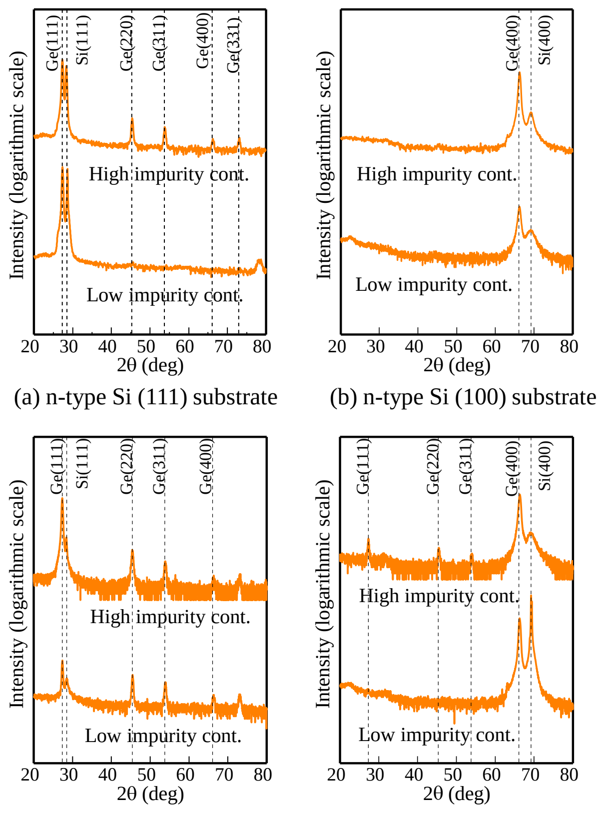
2. Experimental

A-Ge precursors were prepared on n- and p-type c-Si substrates with (100) and (111) orientations by electron beam (EB) evaporation. The substrates temperature was 100°C. The deposition rate of the a-Ge was set at 1.0Å/s and the thickness was 6000-10000Å. Some a-Ge precursors were covered by impurity blocking layers of amorphous Si (a-Si), deposited continuously after the a-Ge deposition to suppress impurity incorporation from the surface. The thickness of the blocking layers was 3000Å. The SPC was done by thermal annealing at 400°C in argon atomosphere for 1-10 hours.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of θ-2θ scans for Ge films crystallized by the SPC at 400ºC on various c-Si substrates. Two kinds of a-Ge precursors were used; relatively high impurity concentrations because of the air-exposed surface and relatively low impurity concentrations by the blocking layers on the surfaces. As shown in fig. 1(b), n-type (100) c-Si substrates are the most suitable for the epitaxial-like growth of Ge, because the epitaxial-like growth can be conducted in relatively high impurity concentrations. But the epitaxial-like growth on n-type (111) and p-type (100) c-Si substrates is disturbed with the a-Ge precursors with high impurity concentrations. On the other hand, random crystallization appears on p-type (111) c-Si substrates even if the impurity concentrations were low.

We evaluated the velocity of the preferential growth on various c-Si substrates in order to clarify the difference among the substrates. The crystallinity was measured by the Raman spectroscopy while the thermal annealing time was changed. The velocity of the epitaxial-like growth is the fastest on n-type (100) c-Si substrates, because the crystallization following the (100) direction is seen after the thermal annealing for 2 hours and thus the epitaxial-like growth appears



(a) n-type Si (111) substrate (b) n-type Si (100) substrate

(c) p-type Si (111) substrate (d) p-type Si (100) substrate

Fig. 1 X-ray diffraction patterns of crystallized Ge on various Si substrates with different crystalline orientations and conductive-types. The oxygen concentrations near the surfaces of the a-Ge precursors were more than 10^{20} cm^{-3} indications for "high impurity cont." and around 10^{19} cm^{-3} for "low impurity cont.".

earlier than that on the other substrates. The high velocity of preferential growth probably enables the epitaxial-like growth even in the high impurity concentration. Then the crystallization velocity becomes slower in the order of n-type (111) and p-type (100) c-Si substrates, because the epitaxial-like growth appears after the thermal annealing for 6 and 8 hours on n-type (111) and p-type (100) ones, respectively. These slower velocities give the opportunities of the random crystalline growth on the n-type (111) and p-type (100) c-Si substrates when the random crystalline formation is enhanced at high impurity concentration. On the other hand, the random crystalline formation occurs earlier than the preferential growth on the p-type (111) c-Si substrates. It is not suitable for the epitaxial-like growth.

We considered the reasons why the epitaxial-like growth is disturbed on the c-Si substrates with the p-type conduction or the (111) direction. In the p-type c-Si, available electrons to form covalent bonds are less, so it might take more time to start the epitaxial-like growth from the surface of the substrate. On the other hand, the preferential growth for (100) direction is probably faster than that for (111) direction, because a number of dangling bonds on the (100) surface is more than on the (111) surface. The two conditions are both good in the growth on the n-type (100) c-Si substrate, so the preferential growth following the substrate direction proceeds more easily. But the two conditions are both bad in the growth on the p-type (111) c-Si substrate, so the preferential growth does not occur.

4. Conclusions

We successfully obtained the epitaxial-like growth of Ge by the SPC from a-Ge precursors on c-Si substrates as seed layers. The n-type c-Si substrate with the (100) orientation is the most suitable for the preferential growth following the substrate orientation, because the growth velocity is faster than that on the other substrates. The SPC c-Ge might be a good candidate for bottom cell materials of multi-junction solar cells.

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