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Influence of the Ge coverage prior to carbonization on the structure of SiC grown on Si(111)

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Abstract. A structural study of SiC layers grown by molecular beam epitaxy on carbonized Si(111) substrates with Ge modified interfaces is reported. Different quantities of Ge were predeposited prior to the SiC growth for comparison. X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS), Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy in both conventional (CTEM) and high-resolution modes (HREM) and selected-area electron diffraction (SAED) have been used to evaluate the structural quality of the SiC layers. SIMS measurements show that, after the epitaxial growth, the predeposited Ge remains at the interface and in the region of the silicon substrate closest to the interface. This observation was confirmed by HREM investigations. The 300 nm-thick SiC layers are subject to a residual in-plane tensile strain of 0.7-0.8 %. The defect structure indicates an enhanced lattice relaxation caused by Ge incorporation into the SiC/Si interface. The grain size tends to decrease as Ge coverage increases. Furthermore, the presence of Ge suppresses the formation of voids at the interface thanks to the formation of a Si/Ge/C alloy interlayer acting as a barrier for the outdiffusion of Si.

Introduction

There have been several attempts to increase the range of materials compatible with Si technologies. Heterostructures of silicon carbide on silicon (SiC/Si) have proven to be useful in micro- and optoelectronic applications and, also, as templates for the growth of SiC or III-group nitrides [1]. The submonolayer and monolayer predeposition of Ge before the carbonization of Si surfaces is a new concept in the growth of SiC on Si with controlled mechanical properties. The idea is based on a recent theoretical prediction [2] according to which the formation of a solid solution of $Si_{1-x-y}C_xGe_y$ at the interface would allow the fabrication of a SiC/Si junction with improved characteristics. The mechanism involved in this approach is that the incorporation of Ge atoms (with a larger volume than C) induces a change of tensile stress in the heterostructure. This leads to a variation in the distribution of defects and dislocations. The SiC/Si heterostructures fabricated with this new method show better electrical properties. Indeed, it has allowed to improve the ideality factor and to decrease the reverse-bias current of n-3C-SiC/p-Si heterojunction diodes [3]. In this report the growth and characterization of SiC/Si structures with different Ge-covered interfaces are presented.

Experimental

300 nm-thick SiC layers were grown by solid source molecular beam epitaxy (SSMBE) on on-axis boron-doped p-type Si(111) wafers in an UMS 500 Balzers MBE system. The detailed growth procedure consists of the steps described elsewhere [3] which basically are the deposition of 0, 0.1, 0.25, 0.5 or 1 ML of Ge plus 6 ML of C at 325°C on the Si (111) surface, a subsequent increase of the temperature and the growth of SiC at 1050°C. In order to study the main features of the SiC/Si heterostructure the following techniques have been used: secondary ion mass spectrometry (SIMS), conventional and high-resolution transmission electron microscopy (TEM), selected-area electron diffraction (SAED), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

Depth profiling by SIMS was carried out with an IMS 4F CAMECA system. An O_2^+ primary beam with impact energy of 14.96 kV was used. The incidence angle was 60°. Specimens were prepared for cross-section TEM (XTEM) and planar-view TEM (PVTEM) using mechanical thinning and Ar^+ milling at 4.5 kV in a Gatan Dual Ion Mill system. Conventional TEM was carried out in a JEOL JEM-1200EX electron microscope; a JEOL JEM-2000EX/THR was used for HRTEM. FTIR spectra with a resolution of 4 cm^{-1} in reflectivity mode were collected with a μ-FTIR Nicolet Impact 410 equipment attached to a FTIR microscope IR Plan Advantage. XRD patterns were measured with a Bede D^3 diffractometer. $\theta/2\theta$ scans were recorded around the (111) and (333) reflections of Si and (111), (222) and (333) of SiC. Pseudo-Voigt functions were fitted to the SiC peaks to deduce the grain size and microstrain of the samples [4]. Rocking-curves (r-c) around the (111), (222) and (333) reflections of SiC were also measured.

Results and discussion

FTIR measurements. Reflectance FTIR allows the direct identification of the SiC layer. The FTIR spectra did not show typical SiC/Si Reststrahlen bands due to the relative good crystalline quality and small thickness of the SiC overlayers [5]. Anyway, the observed peaks proved the good quality of the SiC material. Figure 1 (a) shows two FTIR spectra measured in samples with 0.1 and 0.5 ML of Ge. An isolated peak with a maximum located around 790-800 cm^{-1}, corresponding to the (w_{TO}) "stretching" mode of almost stoichiometric SiC, is observed. In some cases the spectra exhibit a broadening that could indicate a transition to a Reststrahlen band. The measured values are close to the wavenumber observed by other authors for similar structures or bulk SiC (from 794 to 796 cm^{-1}) [6]. The minimum located around 966 cm^{-1} is associated with the LO phonon mode of 3C-SiC (ideally at 971 cm^{-1}). The observed small shifts are related to residual stress in the non-fully relaxed SiC layers. The stress could indicate the presence of defects, disorders, doping effects or the influence of the Si substrate on the interface region [7]. We have not found any relation between the SiC peak positions and the quantity of Ge predeposited but higher resolution Raman and IR ellipsometry experiments showed a shift of TO modes related to the Ge coverage [8].

XRD measurements. From the Bragg angle of the SiC peaks we have deduced the interplanar spacing along the [111] direction (d_{111}), which changes from 2.5128 Å to 2.5133 Å as the Ge coverage varies from 0 to 1 ML. All these values are smaller than the bulk SiC d_{111} value (2.5170 Å). Therefore, the layers are not completely relaxed, but are subject to an in-plane tensile strain (ε_{II}) ranging from 0.79% to 0.69%, as calculated from the values of d_{111} using the conventional elasticity theory. This is shown in Fig. 1(b), together with the variation of the SiC/Si lattice mismatch (*m*) with Ge coverage. Thus, the Ge predeposition reduces the residual mismatch stress of the SiC layer on the Si substrate. The full-width-at-half-maximum (FWHM) of the $\theta/2\theta$ patterns changes from 0.121° to 0.136° as the Ge coverage increases (see Fig. 1(c)). From the shape of the SiC (111) peak it is possible to quantify the grain size in each layer [4]. The grain size decreases as the Ge predeposition increases, ranging from values larger than 1500 Å for Ge coverages below 0.5 ML to 900 Å for 1 ML. The r-c FWHM is similar for all the samples (around 0.7°) except for the sample with 1 ML of Ge (1.1°), as shown in Fig. 1(c). From these results it seems that the incorporation of Ge promotes the relaxation of the SiC layer. At the same time the grain size tends to decrease, which might be due to an increase in the dislocation density as relaxation is enhanced. The reduction of the grain size seems to induce a larger dispersion of the misorientation of the grains, as shown by the increase of the r-c FWHM.

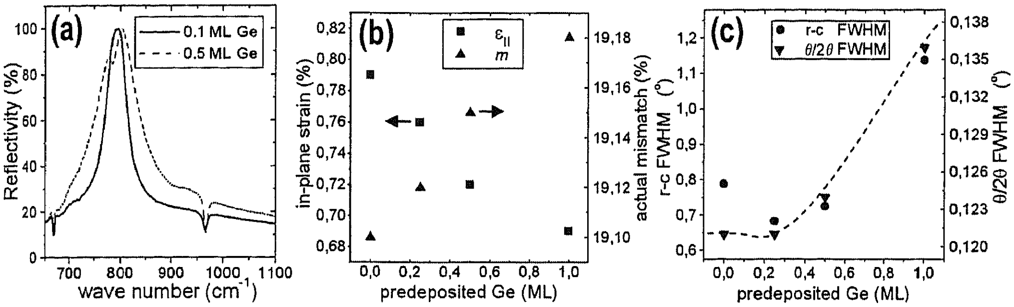

Fig. 1. (a) FTIR spectra for samples with 0.1 and 0.5 ML of Ge; (b) strain and mismatch as a function of Ge predeposition; and (c) θ/2θ FWHM and r-c FWHM for different Ge coverages.

SIMS measurements. A detailed SIMS study of these and other samples can be found in a recent publication [9]. In this section we present a summary of the most important features. The obtained depth profiles show a similar aspect for all the samples, with three different regions from which the SiC layer and the Si substrate can be identified clearly. The interface region is defined through the variation of the Si signal; its thickness is a few nanometres for all the samples. Germanium atoms are located at this interface layer; they diffuse over 30 nm into the Si substrate, having a maximum near the initial Si surface. The amount of detected Ge increases with the predeposition of Ge with a minor contribution of Ge outdifussion. The C distribution inside the Si substrate shows a deep tail with a marked decay that vanishes for samples with 0.5 and 1 ML of Ge. It is confined from the interface region to the limit of the Ge signal indicating a suppressed diffusion by the SiC forming elements. In the case of lower Ge concentrations, the C diffusion into the Si substrate extends beyond the region where Ge is located.

TEM measurements. The β-SiC(111)//Si(111) structures exhibit SiC with good crystalline orientation with respect to the Si substrate. Extended defects were found in all the samples studied by TEM. The SiC layer is partially relaxed as concluded from the SAED analysis carried out for samples prepared in both XTEM and PVTEM orientations. HREM micrographs at the SiC/Si interface show two clear crystalline structures related to the Si substrate and the SiC layer. Besides, a distinct contrast (structure) is observed at the heterointerface. This new structure is not uniform. Its thickness varies between 1 and 3 nm depending on the region studied. It is pseudomorphically grown on the Si substrate since the lattice planes maintain their continuity and a misfit dislocation network is placed just on top of the new structure. This interlayer stops the formation of voids, thus producing a combination of: (a) increased crystalline density, (b) sealing of Si out-diffusion channels, and (c) stress reduction.

In order to study the void suppression a detailed PVTEM study was carried out. The voids size distribution over the Si surfaces in samples without Ge show an exponential decay similar to that previously observed in SSMBE-carbonized Si(001) and Si(111) surfaces (without epitaxial overgrowth of SiC) [10]. Figure 2 (a) is a bright field (BF) XTEM micrograph of the SiC layer with 0.5 ML of Ge. It does not show any voids at the SiC/Si interface.

Other complementary theoretical [2] and experimental [9] studies propose the formation of a new phase corresponding to a $Si_{1-x-y}C_xGe_y$ solid solution. HREM indicates that C and Ge inside the Si substrate at the near SiC/Si interface are interstitially located, since Si lattice planes show similar spacings to those measured in the relaxed bulk Si substrate. Figure 2 (b) shows a HREM image of the sample with 1 ML of Ge. This micrograph shows: (i) the Si/C/Ge alloyed interlayer; (ii) (111) planes associated with relaxed Si; and 3C-SiC structures and (iii) other SiC planes related to misoriented SiC grains. Roughness and surface steps promoted by Ge segregation and diffusion produce threading planar defects (PD) towards the SiC overlayer. The inset shows the diffraction pattern associated to the same specimen. In this SAED pattern registered along the [111] zone axis, reflections due to typical cubic SiC and Si networks perfectly aligned in the same direction indicate good orientation between both crystalline structures. Multiple diffraction produced by the interaction of SiC/Si is also visible.

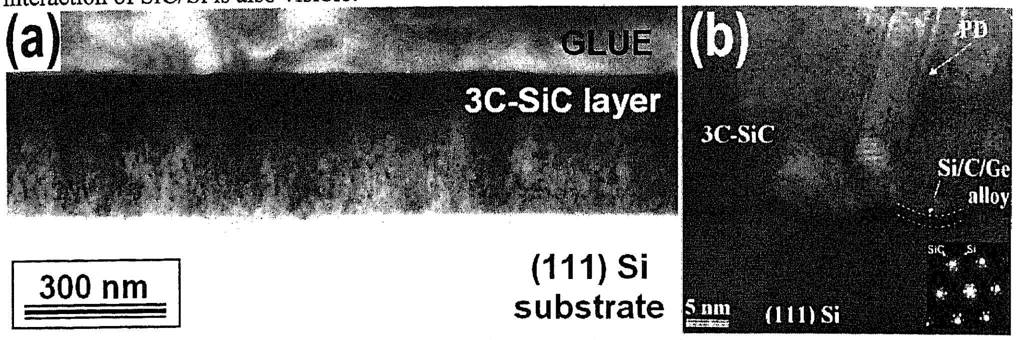

Fig. 2. BF XTEM image of a sample with 0.5 ML of Ge (a) and HREM image of a sample with 1 ML of Ge.

Summary

A multitechnique study has been carried out to investigate β-SiC(111)//Si(111) heterostructures fabricated by predepositing different coverages of Ge. The SiC layers exhibited good orientation and crystalline quality. As Ge predeposition was increased, the SiC layers exhibited lower residual strain and smaller grain size. Ge atoms are located near the SiC/Si interface and do not extend into the SiC layer. The formation of a $Si_{1-x-y}C_xGe_y$ layer at the interface region prevents Si outdifussion and, consequently, the formation of voids.

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