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Formation of β-SiC Nanocrystals by the Relaxation of $Si_{1-y}C_y$ Random Alloy Layers

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In this work $Si_{1-y}C_y$ random alloy is used as a starting point for the creation of nano partices of beta-SiC with the same lattice orientation as the Si lattice in which they are grown. These nano particles are between 3 and 8 nm in diameter and are randomly dispersed throughout the $Si_{1-y}C_y$ region, where $0.005<y<0.05$. This ability to produce quantum antidots of wide bandgap material within the Si matrix should enable the exploration of mesoscopic phenomena.

Introduction

Pseudomorphical growth of $Si_{1-y}C_y$ random alloys on Si (100) substrates has produced thin epitaxial films that are in tension[1]. This tensile strain causes a lifting of the conduction band degeneracy, such that the 2-fold degeneracy with lighter in-plane effective electron mass[2,3] has lower energy. The growth of $Si_{1-y}C_y$ random alloy is kinetically stabilized by growth at low temperatures. This also results in pseudomorphic growth with the Si substrate. The random alloy, however, is unstable and anneals at high temperature form more stable SiC phases. This process has been utilized to create well controlled and uniformly allingned β-SiC crystallites that are dispersed in a crystalline Si or a SiGe matrix.

Growth

The $Si_{1-y}C_y$ material in this work was grown in a solid source MBE system described elsewhere[4]. An elemental graphite filament was heated to a sublimation temperature in excess of 3000K to provide the Carbon flux.

Unlike Ge alloys of Si where the Ge is miscible with the Si, the growth of $Si_{1-y}C_y$ alloys is complicated by the fact that C has a very low solubility in Si, i.e., below 10^{-6}, at 1400K. There are also a number of silicon carbide phases and polytypes which, in equilibrium, form preferentially. To avoid this problem it is necessary to kinetically stabilize the growth by deposition of the $Si_{1-y}C_y$ at low temperatures, i.e., below 550°C. Thus the $Si_{1-y}C_y$ is deposited in a non-equilibrium growth regime[4,5]. At temperatures above this, silicon carbide is found to be the dominant phase and good pseudomorphic growth on Si is no longer possible. However, once the $Si_{1-y}C_y$ random alloy has been deposited it is found that surprisingly high annealing temperatures, (> 900°C), are required in order for the carbide phases to be formed[6].

Experiment

Random alloys of $Si_{1-y}C_y$ with $0.005 < y < 0.05$ were successfully deposited at low temperatures on Si (100) substrates. The strain relaxation was evaluated, first through dislocation formation at lower temperatures and then by precipitation of SiC at higher annealing temperatures. Double crystal X-ray diffraction was used to determine the strain state in the alloy layers. The <113> glancing incidence rocking curve for a y=0.007 sample after 1 hour anneals at different temperatures is shown in Fig. 1. The anneal at 700°C exhibited a 20% relaxation of the epilayer strain, while the sample annealed at 900°C showed a 25% relaxation. This relaxation is to be expected as the layers are above the equilibrium critical thickness for tensile layers, as predicted by Matthews[7], and shown experimentally[2]. As the level of strain in the layer is reduced the driving force on the dislocations decreases and thus the dislocation motion is limited.

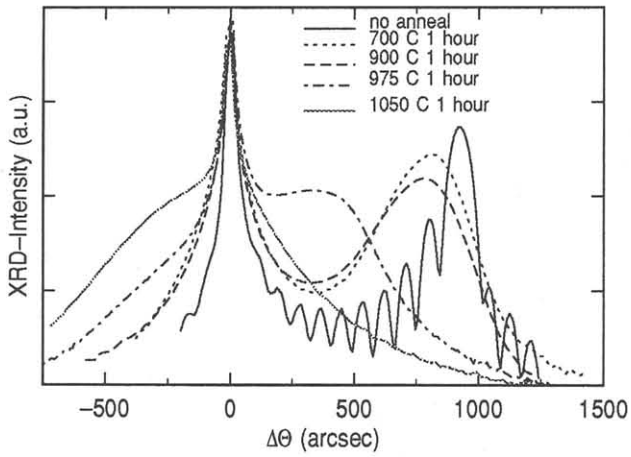

Fig 1. The <113> glancing incidence rocking curves of a 400 nm y=0.007 $Si_{1-y}C_y$ alloy layer are shown for various 1 hour anneals. Clear pendellosung peaks, indicating high quality material, are seen in the unannealed sample. The 700°C and 900°C anneals show some relaxation of strain, and the pendellosung peaks have been washed out due to strain fields associated with dislocations. After 975°C and 1050°C anneals the degree of strain relaxation can only be explained in terms of carbon precipitation.

For annealing temperatures above 900°C further relaxation of the strain occurs. After a 1 hour anneal at 975°C the relaxation in the epitaxial layer is greater than can be accounted for by dislocation generation. For the 1 hour anneal at 1050°C the tensile strain in the layer has been completely removed, this is due to the precipitation of the carbon, the layer is in fact under compressive strain. The compressive strain of 7×10^{-4} i.e., 20% of the original strain, is roughly equivalent the strain relieved by dislocation formation after the 900°C anneal. This fact is confirmed with planar Transmission Electron Microscopy, as shown in Fig. 2 (b), it clearly shows a network of misfit dislocations present after the high temperature anneal. These dislocations are usually formed as the sample is ramped up in temperature to reach the final annealing temperature. They would be expected to annihilate themselves as the carbon precipitates out and removes the tensile strain in the layer. In this case the silicon carbide precipitates acted as blocking points for the dislocations thus locking in the dislocation network, and creating a the net compressive strain in the layer.

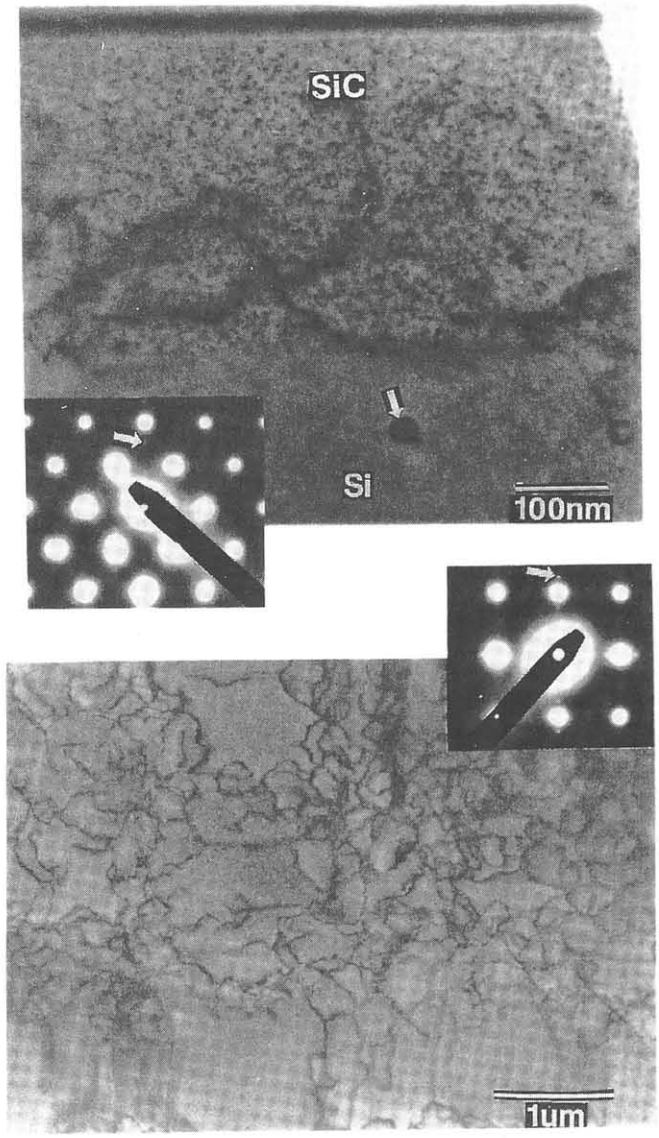

Fig 2 Both TEM images show the 400 nm y=0.007 $Si_{1-y}C_y$ alloy layer after the 1050°C anneal. The upper image is a cross-section view where the dislocations can be seen along with the β-SiC precipitates, also included is the diffraction pattern obtained from this sample. The lower image shows a planar TEM view, here the network of misfit dislocations can be seen, this network was unable to annihilate itself when the tensile strain was removed because, the β-SiC precipitates pinned the dislocations. The highlighted spots on both diffraction patterns are from the β-SiC precipitates.

Fig. 2 (a) shows the SiC precipitates in the epilayer after the 1050°C anneal, these are found to have a diameters in the range of 3 to 5 nm. The diffraction patterns obtained from both the cross-sectional and planar TEM show the main spots from the Si lattice and (highlighted) additional spots from the SiC precipitates. The lattice constant of the precipitates, was determined, from the spacing of the additional spots, to be 0.436 ± 0.005 nm. The spacing and position of the extra spots is consistent with β-SiC where the crystal structure is face centered cubic and the lattice constant, a= 0.439 nm. Since, diffraction spots are obtained, rather than rings, the nanocrystals must all be aligned in the same direction. In this case they are all orientated in the same direction as the Si lattice surrounding the nanocrystals.

There is no strain observable in TEM at the interface and both the nanocrystals themselves and the Si matrix, appear to be free of strain, other than the strain due to the pinned, dislocation network. Thus they may be considered as free particles within the Si matrix. As the nanocrystals are produced after expitaxy has occurred, no new dislocations are created in the Si matrix material. Thus when $Si_{1-y}C_y$ layers below the equilibrium critical thickness are used, no dislocations are observed to thread in the Si matrix material, in the post annealed layers .

Examination of other $Si_{1-y}C_y$ samples with y ranging from 0.005 to 0.05 shows an increase in nanoparticle size from an average of 3 nm for x=0.005 material to 7 nm for x=0.05 alloy after the high temperature anneal. This suggests that the size of the nanocrystal is diffusion limited as, on average, the precipitates appear to consist of the C collected from a sphere of radius ~10nm surrounding the precipitate. Thus when the initial alloy composition is y_1=0.005 we see precipitates approximately($3\sqrt{\ y_2/y_1}$) i.e., 2.2 times smaller than those seen for a structure with alloy composition y_2 = 0.05. Whether the density and hence the size of these nanocrystals depends upon the annealing temperature used, or on the diffusion constant at the temperature at which the β-SiC first starts precipitating is unclear, and requires further annealing studies.

Conclusions

We have examined the stability of the $Si_{1-y}C_y$ alloys in terms of their behavior during high temperature annealing. We find that the $Si_{1-y}C_y$ random alloy evolves into an array of β-SiC nanocrystallites at high temperatures. These particles have uniform size and orientation. This orientation is the same as the Si matrix in which the β-SiC nanocrystals are imbedded. We are able to control the terminal size of these nanocrystals by adjustment of the original random alloy composition. In addition the z direction positioning of nanopartical layers is controlled from the original structure of the $Si_{1-y}C_y$. Thus we have produced strain free nanocrystals of β-SiC in high quality epitaxial Si material .

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