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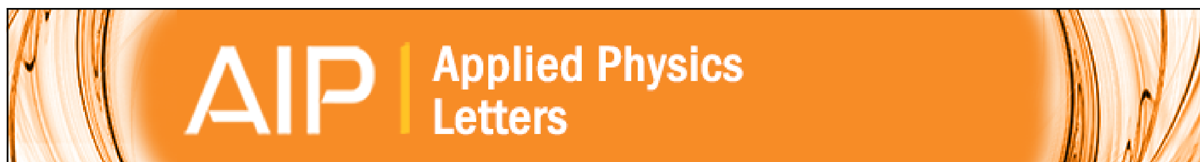

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APPLIED PHYSICS LETTERS **86**, 152113 (2005)

Evidence of formation of Si–C bonds during growth of Si-doped III–V semiconductor compounds

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In this work, we demonstrate that Si–C bonds are formed in III–V semiconductor compounds grown by chemical beam epitaxy. Our results suggest that the formation of Si–C bonds occurs in III–V epitaxial layers with acceptor Carbon residual concentration and high Si concentrations ($>10^{17}$ cm^{-3}). The main consequence of Si–C bonds is the generation of defects along [111] direction. These defects produce carrier concentration saturation, reduction of electrical mobility, crystal quality degradation, and surface defects. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1905783]

Silicon is a commune impurity used as a shallow donor in III–V semiconductors grown by molecular beam epitaxy and chemical beam epitaxy (CBE). A sticking coefficient close to 1 and low memory effect make it preferable to others as a donor dopant for most III–V materials.[1] However, some problems have been observed for large Si concentrations. For example, it has been shown that carrier concentration saturation occurs in layers grown by CBE.[2–4] Thus, above a certain Si effusion cell temperature, carrier concentration remains constant while Si concentration increases.

In this work, we present and discuss the effects of high Si concentration in the InGaP and GaAs layers lattice matched to GaAs grown by CBE. We have used arsine, phosphine, triethylgallium, and trimethylindium as arsenic, phosphorus, gallium, and indium sources, respectively. The growth temperature was varied between 500 and 540 °C. A solid Si in an effusion cell has been used as the Si source, with cell temperature varied in the range 1000–1200 °C.

Figure 1 shows the Hall carrier concentration as a function of reciprocal temperature of the Si cell for three growth temperatures: 500, 520, and 540 °C. Si concentration measured by secondary ion mass spectroscopy (SIMS) is shown for the sample grown at 500 °C. As can be seen, for the samples grown at 500 and 520 °C, the carrier concentration saturates around 4×10^{18} cm^{-3} and 8×10^{18} cm^{-3}, respectively. On the other hand, for the sample grown at 540 °C there is no saturation in the studied temperature range. For samples grown at 500 °C, SIMS results show that Si incorporation can be described by an exponential curve (as well Si vapor pressure) in the entire temperature range. This indicates that part of incorporated Si is not electrically active or not incorporated as donor.

Figure 2 shows the x-ray diffraction measurements for heavily Si-doped samples grown at different growth temperatures. For the peak corresponding to InGaP, we observe significant full width at half maximum (FWHM) enlargement from 80 to 400 arc sec and a shift towards smaller lattice constant when its growth temperature decreases from 540 to 500 °C. Extra peaks appear at 520 and 540 °C, the InGaP peak becomes very large. This peak enlargement is an indication of crystal quality degradation for samples grown at lower temperatures. This indication is corroborated by observed surface morphologies of higher Si doped samples (not shown here). The surface of the sample grown at 500 °C presents structures like grains. These structures can be easily observed in Normaski optical micrographs as sand-like morphology. The grains are smaller in size and density for the sample growth at 520 °C than sample growth at 500 °C. For the sample growth in 540 °C the surface is almost flat. These results indicate defect formation in the InGaP layers and a raise in density when growth temperature is reduced.

A possible cause for defect formation is the residual carbon incorporation. For example, it has been shown[5] that for high growth temperatures (~560 °C) most of the carbon atoms are incorporated as donors—therefore replacing III group atoms—and for low growth temperatures (~500 °C), C incorporates as acceptors—therefore replacing P atoms.

Surface diffusion of atoms on a growing surface is usually described by an Arrhenius expression for the hopping rate.[6] Larger diffusion rates of Si atoms are expected to occur at usual CBE InGaP growth temperatures (500–560 °C). Since Si and C are both present on the surface, the Si–C bond formation should occur where Si is incorporated as donor and C is incorporated as acceptor. In this sense, we should expect a higher rate of Si–C bond formation for lower growth temperatures, which have higher C incorporation as acceptor.

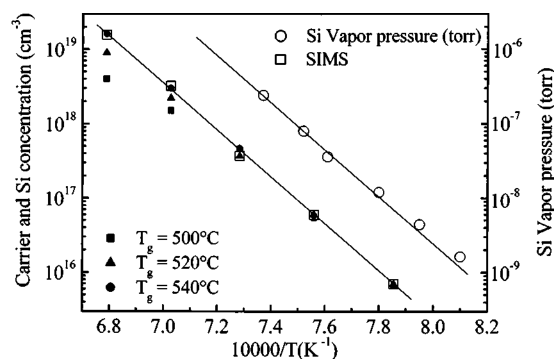

FIG. 1. 300 K Hall concentration for InGaP:Si samples grown at 540, 520, and 500 °C as a function of inverse Si cell temperature. Si concentration measured by SIMS as function of Si cell reciprocal temperature for sample grown at 500 °C. In this figure, Si vapor pressure as function of its reciprocal temperature is shown too.

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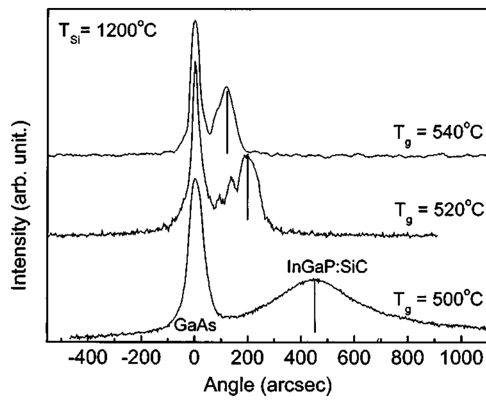

FIG. 2. Rocking curve for samples grown at three different temperatures: 540, 520, and 500 °C. The Si cell temperature was kept at 1200 °C. InGaP layers are 2 μm thick.

Si atoms bond to the C atoms became electrically inactive what can be linked to saturation observed at Fig. 1. Besides this, the SiC structure is cubic and the lattice parameter is closely twice lower than InGaP. If Si–C bonds are formed during growth and assuming that Si–C bonds are lower than III–P bonds, a reducing in the lattice parameter and the FWHM enlargement observed in Fig. 2 should be expected when growth temperature decreases.

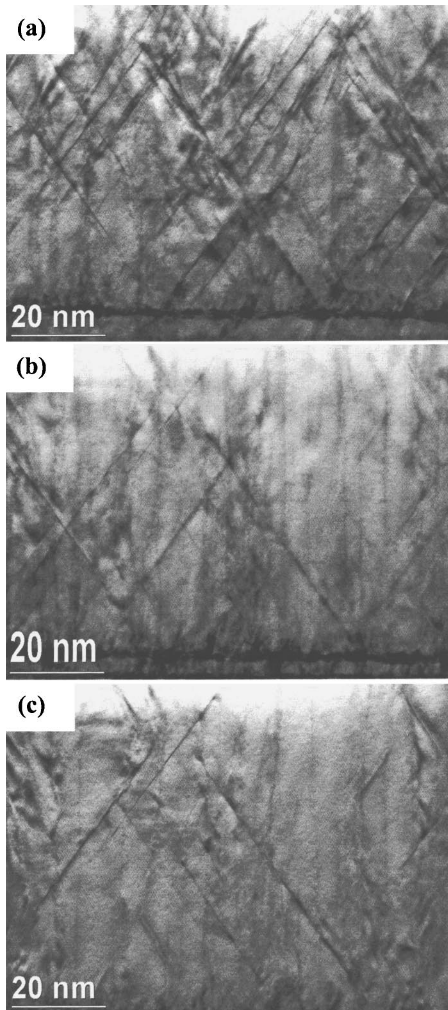

FIG. 3. [110] bright-field images of the InGaP:Si layers grown at (a) 500, (b) 520, and (c) 540 °C keeping T_{Si}=1200 °C.

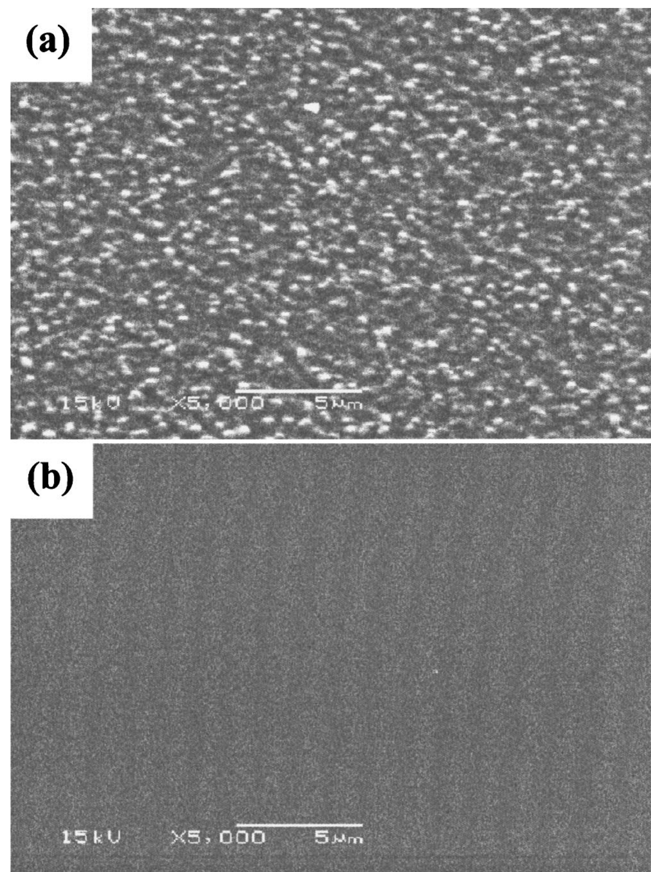

FIG. 4. SEM images of the surfaces of GaAs:Si samples grow with T_{Si} =1200 °C and (a) C residual incorporated mainly as acceptor and (b) as donor.

As Si–C presents directional bond at [111], it can suppose misfit dislocations along of [111] directions. To analyze the defect formation transmission electron microscopy [110] bright-field images have been used as is shown in Fig. 3. Misfit dislocations along [111] direction are observed for all samples. The density of such dislocations decreases as growth temperature increases. This feature suggests that Si–C bond formation decrease as growth temperature increases.

It is well know that, the residual carbon incorporation in CBE grown GaAs layers depends on growth conditions. For the GaAs samples grown in the studies, most of the carbon is incorporated: (a) as acceptor for sample grown at higher growth temperature (560 °C) and low V/III ratio (~5), (b) as donor for sample grown at lower growth temperature (500 °C) and high V/III ratio (~50).

In order to verify the presented hypothesis, Si-doped GaAs layers have been grown using T_{Si}=1200 °C at (a) and (b) growth conditions. Figure 4 shows the scanning electron microscopy (SEM) images for these samples. It was observed that the sample grown at (a) condition presents surface degradation, while sample grown at (b) condition does not. Other characteristics were observed as well: the electron concentration was 2×10^{18} cm^{-3} for samples grown at (a) condition and 2×10^{19} cm^{-3} when at (b) condition, indicating electron concentration saturation for sample grown at (a) condition. Also, the FWHM of x-ray measurements show an increase of an order magnitude (enlargement from 22 to 215 arc sec) and a shift towards smaller lattice constant for sample growth in (a) condition relative to that grown in (b)

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condition. Thus, GaAs samples present similar behavior observed for InGaP layers as expected by our hypothesis.

In summary, we propose that during growth Si-doped InGaP (or GaAs), Si–C bonds are formed when high Si concentrations ($>10^{17}$ cm^{-3}) and carbon ($>10^{17}$ cm^{-3}) are attained. This process is responsible for defects generation along [111] direction.

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