Microchim. Acta 145, 165–169 (2004)
DOI 10.1007/s00604-003-0147-5

Microchimica Acta
Printed in Austria

Original Paper

Crystalline Inclusions Formed in $C + N + BF_2$ Coimplanted on Silicon (111)

Arturo Ponce[1,*], **Francisco M. Morales**[1], **Sergio I. Molina**[1], **Lucía Barbadillo**[2], **Manuel Cervera**[2], **Marí J. Hernández**[2], **Pedro Rodríguez**[2], and **Juan Piqueras**[2]

[1] Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, E-11510 Cádiz Spain
[2] Laboratorio de Microelectrónica, Facultad de Ciencias, Universidad Autónoma de Madrid, E-28049 Madrid Spain

Received May 22, 2003; accepted October 20, 2003;

Abstract. In the present work, high-doses (10^{17}–$10^{18}\,cm^{-2}$) of carbon, nitrogen, and boron (BF_2^+) ions were coimplanted on silicon (111) substrates at 21, 25 and 77 keV, respectively. Two series of samples have been implanted (series A and B) and subsequently annealed. Series A samples have been implanted at room temperature and treated one minute by rapid thermal annealing (RTA) and 3 hours at 1200 °C. Series B samples have been implanted at 600 °C and subsequently annealed at 1200 °C during 3 hours. The annealing in both series has been carried out in N_2 at atmospheric pressures.

The structure of the buried layers has been determined by conventional and high resolution transmission electron microscopy (CTEM and HRTEM). Polycrystalline silicon and new crystalline phases are observed by electron diffraction patterns. The polycrystalline silicon inclusions have been confirmed from analysis of HRTEM images.

Key words: Coimplantation; transmission electron microscopy; annealing; crystalline inclusions.

During several decades, the ion implantation process has been used for doping semiconducting materials. The addition of simultaneous species coimplanted at high doses can produce the formation of new crystalline phases layers, which are grown on the surface or buried in the substrates. Carbon, nitrogen and boron species, can be coimplanted on silicon substrates in order to obtain crystalline phases like BN or BC_2N, Si_3N_4, C_3N_4 or SiC. Each crystalline phase possesses different micro and optoelectronic properties [1–5]. After an annealing process, these crystalline phases can transform in other phases or disappear. On the other hand, thermal annealing of the physical damage resulting from the implantation process can result in the generation of defects. The conventional coimplantation is carried out at room temperature. However, the *in-situ* ion implantation at high temperature is a relatively novel process [6]. Coimplanted species are distributed in different forms depending on temperature, energy, dose and species of coimplantation.

In previous work, we have reported the existence of new crystalline phases on silicon after binary coimplantation processes, which were carried out at room temperature and 600 °C [6, 7]. The species in these binary coimplantation processes were $C^+ + N^+$ and $BF_2^+ + N^+$. The mentioned phases have been detected by conventional and high transmission electron microscopy (CTEM and HRTEM, respectively) using selective area electron diffraction (SAED) patterns and Moiré analysis. The detected phases were generally C_3N_4, SiC, Si_3N_4, and polycrystalline silicon. Twin

---

[*] Author for correspondence. E-mail: arturo.ponce@uca.es

Table 1. Summary of implantation conditions

Sample	Ion implantation dose ($\times 10^{17}\,cm^{-2}$)/energy (KeV)			Implantation temp. (°C)	Annealing time/temp. (°C)
	C^+	N^+	$BF_2{}^+$		
A1	5/21	5/25	3/77	~25	RTA (1 min)/1200
A2	5/21	5/25	3/77	~25	3 h/1200
B1	5/21	5/25	5/77	600	as implanted
B2	5/21	5/25	5/77	600	3 h/1200

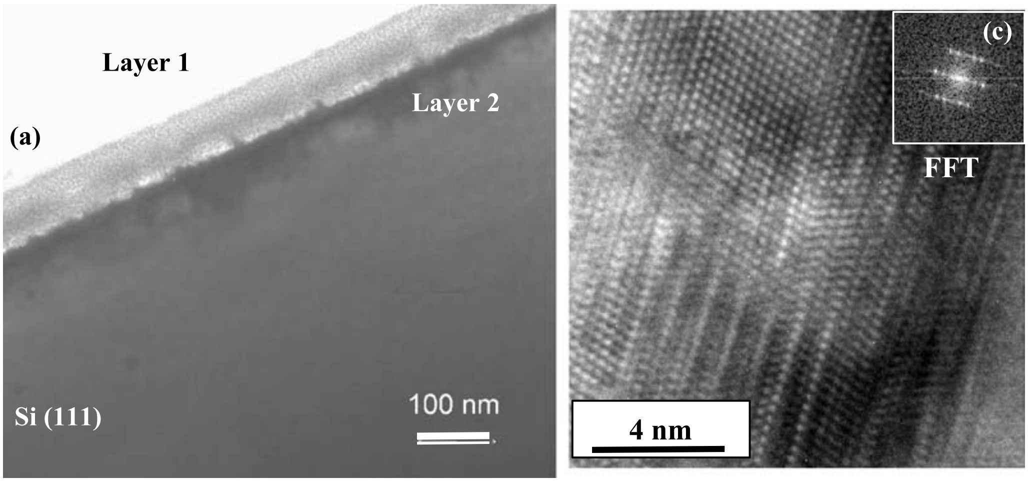

Fig. 1. (a) Bright field XTEM image registered in [110] axes zone for sample A1. (b) HRTEM image of layer 2 of sample A1

and planar defects have been observed for 600 °C-coimplanted samples.

In the present work, high-doses (10^{17}–$10^{18}\,cm^{-2}$) of C^+, N^+, and $BF_2{}^+$ ions were coimplanted on silicon (111) substrates at 21, 25 and 77 keV, respectively. Two coimplantation temperatures have been used (room and 600 °C).

Experimental

In order to perform the coimplantations, both-sides-polished (111) float-zone silicon substrates (n-type, doped with phosphorus concentration about $10^{14}\,cm^{-3}$) have been used. Carbon, boron and nitrogen species have been coimplanted in a modified Varian-Extrion ion implanter. The ion-current densities were about $5.6\,\mu A \cdot cm^{-2}$ for N^+, $3\,\mu A \cdot cm^{-2}$ for C^+, and between 7.5 and $11\,\mu A\,cm^{-2}$ for $BF_2{}^+$. Implantation conditions (dose and energies) are summarized in Table 1. Energies were selected to obtain a projected range of about 650 Å, as deduced using the SRIM program [8]. Doses were chosen to obtain a peak concentration of the implanted ions similar to the bulk silicon density, $5 \times 10^{22}\,cm^{-3}$. Two series of samples have been coimplanted at room temperature (A) and at 600 °C (B). In series A samples, the sample holder was cooled by a closed-cycle cooling system, while in series B samples, the temperature of the sample holder has been maintained at 600 °C with a controlled hot filament furnace. Afterwards, all coimplanted samples were annealed in pure nitrogen atmosphere.

TEM studies were carried out in the JEM 1200-EX (for CTEM studies) and JEM 2000-EX (for HRTEM studies) microscopes, which operate at 120 kV and 200 kV, respectively. Cross-sectional TEM (XTEM) specimens were prepared by mechanical thinning approximately to 100 μm, subsequently the electron transparency was achieved by ion milling at 4.5 kV with a N_2 liquid cold stage to reduce the damage in the samples.

Results and Discussion

All samples exhibit two layers, the first one on the surface (layer 1) and the second one buried (layer 2) in the silicon substrate. From SAED patterns, is possible to observe a generalamorphous matrix with some crystalline inclusions in layer 1 and a typical twinned

Table 2. Layer thicknesses measured in XTEM images for series of samples A and B

Sample	Layer thicknesses (nm)		
	Layer 1	Layer 2	Total
A1	84 ± 6	45 ± 15	129 ± 21
A2	96 ± 6	25 ± 6	121 ± 12
B1	75 ± 14	100 ± 20	175 ± 34
B2	72 ± 13	52 ± 12	124 ± 25

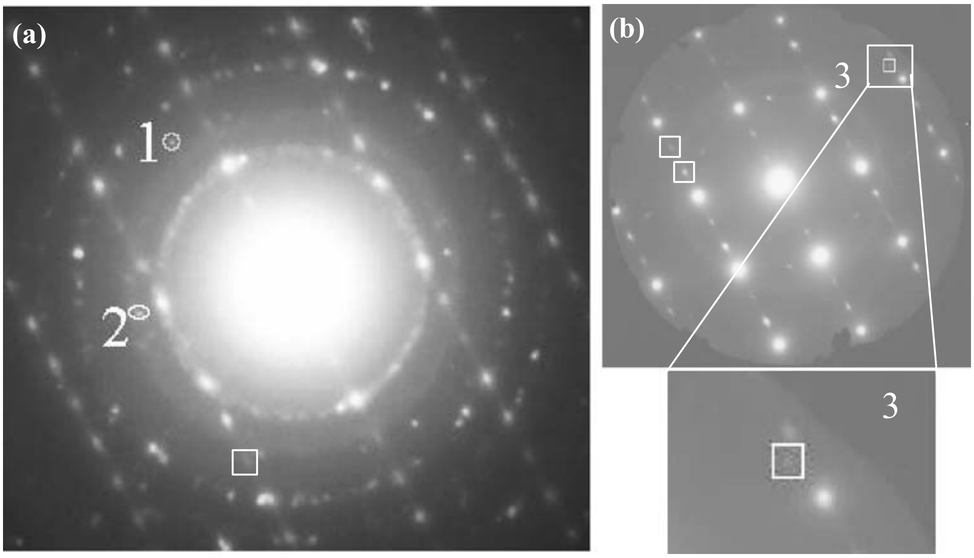

Fig. 2. SAED patterns registered in [110] axes zone of substrate for the samples (a) A1 and (b) A2. The reflection amplified correspond to new crystalline phases inclusions in layers. The squares represent the silicon microtwins

Table 3. Interplanar distances obtained from indexed reflection of SAED patterns of Fig. 2 for A1 and A2 samples. The reflection 1 and 2 correspond to A1 sample and reflection 3 correspond to A2 sample

Reflection from Fig 2 SAEDs/crystalline phase	Associated reflections		Corresponding planes
	Measured interplanar distance (nm)	Theoretical interplanar distance (nm)	
1/β-C_3N_4	0.2252 ± 0,0018	0.2250	(101), (011), ($\bar{1}$01), ($\bar{1}$11), (1$\bar{1}$1), (0$\bar{1}$1)
2/β-Si_3N_4	0.2670 ± 0,0024	0.2663	(101), (011), ($\bar{1}$01), ($\bar{1}$11), (1$\bar{1}$1), (0$\bar{1}$1)
2/2H-SiC		0.2664	
2/4H-SiC		0.668	
3/α-Si_3N_4	0.1638 ± 0,0012	0.1637	(203), (023), ($\bar{2}$03), ($\bar{2}$23), (2$\bar{2}$3), (0$\bar{2}$3)

silicon in the layer 2 [9]. In Fig. 1a, a XTEM image of A1 sample is showed. Likewise, a HRTEM image of the layer 2 is showed in Fig. 1b, the Fourier Fast Transform (FFT) image has been inserted.

Due to the annealing treatment, the total layer thicknesses of both layers decreases slightly. Layer thicknesses are summarized in Table 2.

For series A samples, some crystalline inclusions are detected from SAED patterns analysis. In Fig. 2 two SAED patterns are showed, which correspond to samples A1 (Fig. 2a) and A2 (Fig. 2b). In these SAED patterns some extra reflections associated with silicon microtwins appear. (The squares inserted in the images represent the silicon microtwins generated from ion implantation in layer 2). The extra spots, which don't correspond with any silicon reflection, are indexed with (using EMS program [10]) several possible new crystalline phases: Si, h-BN, c-BN, 2H-SiC, 3C-SiC, 4H-SiC, 6H-SiC, 8H-SiC, α-Si_3N_4, β-Si_3N_4, α-C_3N_4, β-C_3N_4 and BC_2N. The crystalline phases associated with the reflections observed in Fig. 2 are summarized in Table 3. The reflections 1 and 2 (indicated in Fig. 2a) correspond to sample A1, while the reflection 3 (indicated in Fig. 2b) corresponds to sample A2. Evolution of crystalline phases is observed when the sample is annealed for 3 hours. For sample A1 (RTA annealed for 1 minute), the reflection 1 can be assigned to C_3N_4 crystalline phase, while reflection 2 is assigned to β-Si_3N_4, 2H-SiC or 4H-SiC crystalline phases. In sample A2 (annealed for 3 h), the reflections observed in sample A1 disappear and other new reflection appears, which is associated with α-Si_3N_4 crystalline phase.

On the other hand, HRTEM analysis of polycrystals inserted in the amorphous matrix of layer 1

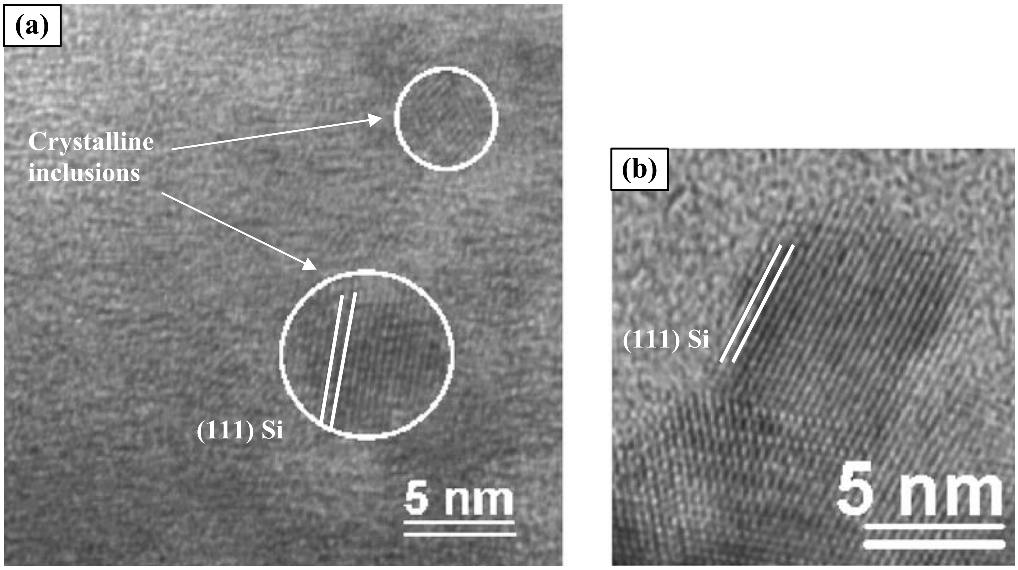

Fig. 3. HRTEM image of a Si crystalline inclusions in layer 1 of samples (a) A1 and (b) A2

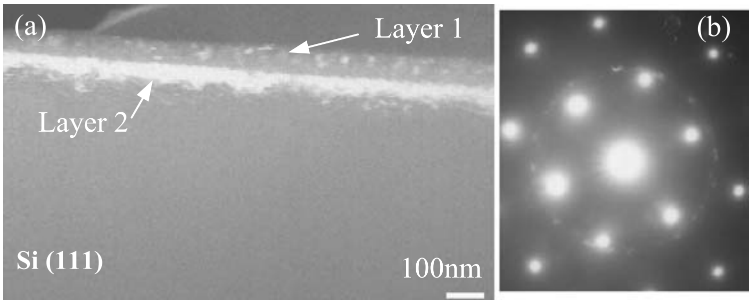

Fig. 4. (a) Bright field XTEM and (b) SAED pattern of sample B2 registered in [110] axes zone of substrate

confirm the existence of silicon polycrystals. New crystalline phase have not been confirmed by HRTEM. In Fig. 3, two HRTEM images of some silicon polycrystalline inclusions are observed in layer 1 of samples A1 (Fig. 3a) and A2 (Fig. 3b). The marked planes in the images, correspond to (111) silicon. The area of polycrystalline inclusions inserted in layer 1 has been estimated from HRTEM images, which is approximately 21% of the layer. Regions of Si underneath layer 2 consist of defect-free monocrystalline Si.

In series B samples, which have been coimplanted at 600 °C, crystalline phases different that silicon have not been detected. Polycrystalline silicon has only been detected in both layers (layers 1 and 2). In Fig. 4a, a XTEM image of sample B2 is showed, where the existence of the two layers (1 and 2) is clearly observed. The SAED pattern corresponding to sample B2 is showed in Fig. 4b, only the existence of polycrystalline silicon is confirmed.

Conclusions

In conclusion, coimplantation of C^+, N^+ and $BF_2{}^+$ on Si (111) substrates at room temperature and 600 °C, originate particular changes in the surface of the substrates. In room temperature coimplantations, new crystalline phases (β-C_3N_4, α and β-Si_3N_4, 2 and 4H-SiC) are detected. New crystalline phases have not been detected in samples implanted at 600 °C.

Acknowledgements. This work has been financed project MAT 2000-0478-P4-02 and the Junta de Andalucía (Group TEP-0120). TEM measurements were carried out at the 'División de Microscopía Electrónica, SCCYT (Universidad de Cádiz)'. A. Ponce is grateful for the support of the *Agencia Española de Cooperación Internacional* (AECI) under a financial MAE grant.

References

[1] Taylor C A, Brown S W, Subramaniam V, Kidner S, Rand S C, Clarke R (1994) Appl Phys Lett 65: 1251–1253

[2] Watanabe M O, Itoh I, Mizushima K, Sasaki T (1996) Appl Phys Lett 68: 2962–2964

[3] Zappe S, Obermeier E, Stoemenos J, Moller H, Krotz G, With H, Skorupa W (1999) Mater Sci Eng B 61: 522–525

[4] Murzin I H, Tompa G S, Wie J, Muratov V, Fischer T E, Yakovlev V (1997) Mat Res Soc Symp Proc 438: 569–574

[5] Tagliente M A, De Carlo L, Tapfer L, Waltereit P, Brand O, Ploog K H (2002) J Appl Phys 92: 70–76

[6] Barbadillo L, Cervera M, Hernández M J, Rodríguez P, Piqueras J, Molina S I, Ponce A, Morales F M (2003) Appl Phys A76: 791–800

[7] Morales F M, Molina S I, Ponce A, Araújo D, García R, Barbadillo L, Cervera M, Piqueras J (2003) Thin Solid Films 426: 16–30

[8] Ziegler J F (1996) SRIM program. IBM Research, Yorktown Heights, NY

[9] Hirsch P, Howie A, Nicholson R B, Pashley D W, Whelan M J (1977) Electron microscopy of thin crystals. Robert E.K. Publishing Co., London

[10] Stadelmann P (1987) Ultramicroscopy 21: 131–145