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Interrupted cycle chemical beam epitaxy of gallium phosphide on silicon with or without photon assistance

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Abstract

The low temperature epitaxial growth of Si–GaP heterostructures by chemical beam epitaxy (CBE) and interrupted cycle chemical beam epitaxy (ICCBE) on patterned partially SiO_2 masked silicon substrates is investigated to achieve dielectric isolation layers for Si circuits as well as for optical interconnections. Excellent selectivity of the growth on exposed Si windows versus SiO_2 covered surface areas is observed and verified by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). Low temperature processing is essential to minimize interdiffusion and strain due to substantial mismatch of the thermal expansion coefficients of GaP and Si. We describe the deposition of GaP by CBE and ICCBE using sources of tertiarybutylphosphine (TBP) and triethylgallium (TEG) on (100) silicon at 310°C and the influence of photon assistance on the growth temperature and surface morphology. Secondary ion mass spectroscopy (SIMS) studies reveal that no measurable interdiffusion occurs under these conditions, including subsequent processing steps that require rapid thermal annealing for 30 s at 900°C. The GaP/Si interface is examined by high resolution cross-sectional transmission electron microscopy (HRTEM) before and after the 900°C anneal.

1. Introduction

Our goal is the use of GaP for dielectric isolation of Si in Si/GaP/Si heterostructures. Low temperature growth is required to avoid interdiffusion and limit stress at the interfaces. Also, the possible use of epitaxial GaP on Si for optoelectronic applications is of interest in the context of optical interconnections [1,2]. We have reported the growth kinetics (shown in Fig. 1) of GaP from TEG and TBP with a fall off in our growth rate below 260°C [3,4]. TEG and TBP were chosen as source materials because of their relatively low pyrolysis temperatures as compared to alternate source materials [5–7]. Yoshimoto et al. reported an enhancement of GaP CBE growth at low temperatures upon exposure of the substrate to a nitrogen laser beam [1]. Precracked phosphine and TEG were used as source beams in this work. The enhancement of the growth rate was attributed by Yoshimoto et al. to photon assisted cracking of the TEG molecules even though they noted that TEG shows no absorption in the wavelength range of the nitrogen laser [1]. The UV absorption of TEG be-

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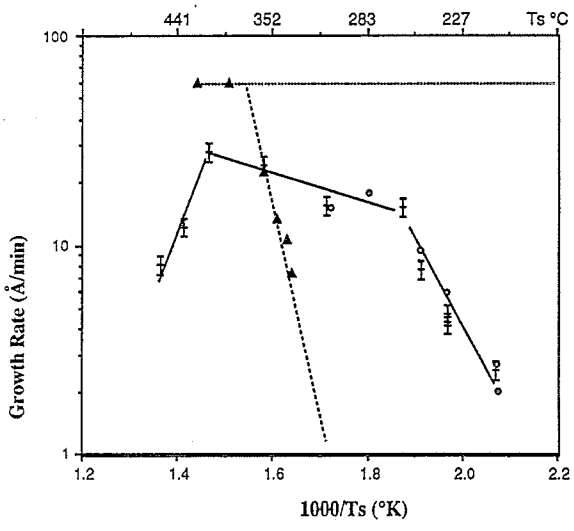

Fig. 1. Temperature dependence of growth rate of GaP from TEG and TBP for (100) silicon substrates. Photon assistance did not significantly increase the growth rate. (+) (100) silicon TBP/TEG = 25; (○) photon assisted TBP/TEG = 25; (▲) PH_3 +TEG [14]; ..... photon assisted PH_3 +TEG [14].

tween 25 and 200°C was found to have a maximum peak at 195 nm and with no absorption above 240 nm [8]. The absorption of TEG at temperatures above 200°C decreases corresponding to the onset of thermal decomposition. Without enhancement by the presence of phosphine fragments on the surface, TEG decomposes on a (100) silicon surface between 227–327°C [6]. UV absorption of TBP has been examined at a pressure of 0.6 Torr in the range of 180–260 nm, peak cross-section absorption was found at 190 nm, at longer wavelengths the absorption fell off [9]. The temperature-pressure dependency of the UV absorption of TBP is unknown at the present time. The presence of TBP enhances the decomposition of TMG and the decomposition of TBP is enhanced by a GaP surface [10]. In this paper, we report the effect of photon assistance on the growth of GaP on Si(100) substrates by CBE and ICCBE processes using TEG and TBP below 260°C.

A feasibility study to determine if phosphorus or gallium from the GaP film after deposition would diffuse into the silicon substrate was examined by SIMS and HRTEM. The GaP films received a 900°C anneal used in advanced silicon device fabrication to relieve stress from oxidation.

2. Experimental

The CBE system was designed with an UV optical window (UV fused silica) position under the substrate holder. The system and processes are described elsewhere [11,12]. The quartz window allows 90% transmission of wavelengths to 200 nm. Two light sources were employed, a nitrogen dye laser, at 337.1 nm with maximum average power of 5 mW and maximum repetition rate of 50 Hz and a 1000 W Hg lamp where the spectral irradiance curve falls off at ~ 220 nm. At the beginning of the run, the TBP is introduced below a substrate temperature of 160°C and the light source is focused on the sample. The light remains on for the entire deposition process and is turned off after depleting the TBP at the end of the run.

Diffusion of phosphorus and gallium from the GaP film after deposition into the silicon substrate was examined by SIMS. Boron doped silicon substrates received an RCA clean and BOE dip (10:1 ammonium fluoride : hydrofluoric acid). The process conditions for the GaP film by CBE were 310°C with a flow rate ratio of $R_{TBP/TEG} = 25$ for 60 min producing a 750 Å film. A 100 Å silicon epitaxial film was grown by remote plasma enhanced chemical vapor deposition (RPECVD) [13]. The process conditions were 50 W and 400°C for 15 min and a gas source of 10% silane in helium. A 1000 Å SiO_2 layer was then grown on top of the silicon to cap the Si/GaP/Si structure. Process conditions for the SiO_2 were 300°C and 15 W with gas sources of 10% silane in helium and nitrous oxide. Fig. 2 is a schematic drawing of the Si/GaP/Si/SiO_2 struc-

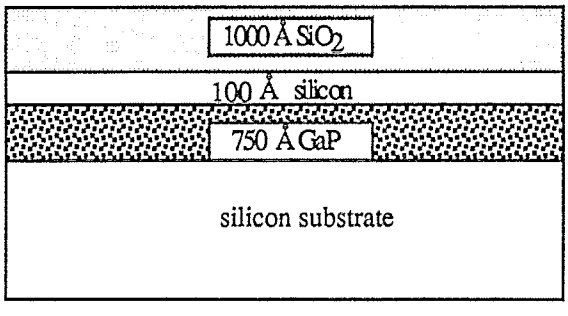

Fig. 2. Stack 1000 Å SiO_2/100 Å Si/750 Å GaP/silicon substrate for diffusion experiment. SiO_2 and the silicon layer were grown by PRECVD and the GaP was grown by CBE.

ture. The samples were cleaved in half and flash annealed at 900°C for 30 s in argon. The SiO_2 and silicon layers were removed and SIMS analyses for carbon, oxygen, silicon, gallium and phosphorus were performed using a CAMECA IMS-4f double focusing, magnetic sector ion microanalyzer with a 14.5 kV, 11 nA Cs^+ primary beam. Samples of the Si/GaP/Si double heterostructure were examined by high resolution cross-sectional transmission electron microscopy (HRTEM) before and after the 900°C anneal.

3. Results

The GaP films grown were selective on silicon areas and did not deposit on SiO_2 covered regions as determined by SEM and AES. No significant increase in the growth rate was observed below 260°C by the addition of either light source to the growth process as seen in Fig. 1. Rutherford backscattering spectroscopy (RBS) of films deposited below 240°C with or without photon assistance reveal the films are deficient in phosphorus. Lowering the substrate temperature to 200°C, gallium is, but phosphorus is not detected by RBS without any clear cut indication for enhanced Ga production in the presence of UV light. The GaP films grown at 310°C with photon assistance did not produce any difference in the surface roughness.

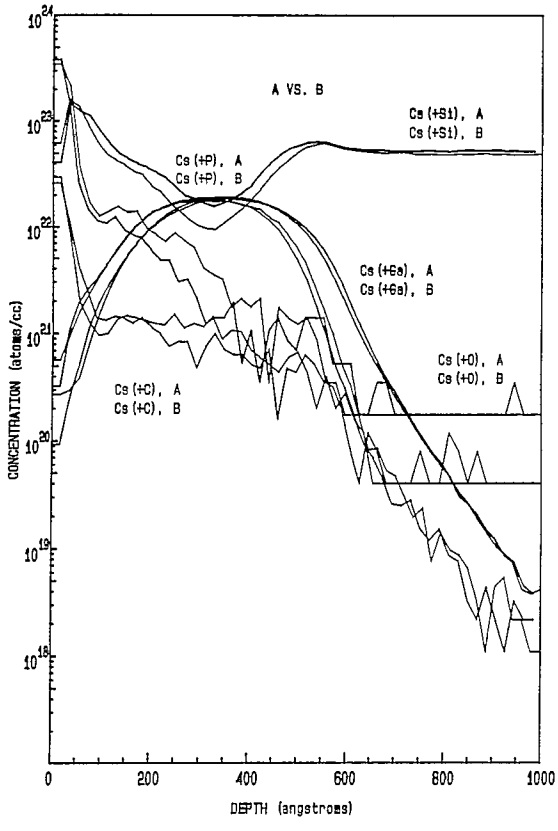

Fig. 3. SIMS processed data comparing annealed and unannealed samples with the GaP film left on. The traces for silicon, phosphorus, gallium, oxygen and carbon are identical and show no diffusion of either gallium or phosphorus into the silicon substrate.

The SIMS profiles for the unannealed and annealed samples are seen in Fig. 3 and the traces for silicon, phosphorus, gallium, oxygen and carbon are identical. The SIMS profile label A is for the unannealed sample, and the SIMS profile label B is for the annealed sample. Gallium and phosphorus did not diffuse into the silicon substrate. The silicon signal does show a dip in the signal at the interface, the higher concentration of silicon at the beginning of the SIMS analysis is probably due to the incomplete removal of the SiO_2 and silicon layers from the samples. The oxygen and carbon signals have more noise than the gallium or phosphorus signals but are very similar and do not show any effect from the anneal. HRTEM did not reveal any difference at the GaP/Si interface between the annealed and unannealed samples.

4. Discussion

The selectivity of the GaP to silicon and not SiO_2 covered regions may be understood due to the presence of a lone pair of electrons on the P atom of the TBP molecule that allows for dative bonding to the silicon surface atoms. For silicon atoms that are backbonded to oxygen, dative bonding becomes highly unlikely, explaining the observed excellent selectivity of GaP growth with regard to SiO_2 covered silicon surfaces. High selectivity is a desirable property in the context of single wafer processing of Si ICs.

The decreased growth rate of our films below 260°C is due the reduction in the decomposition rate of the TBP. A fall off in the growth rate below 260°C is due to the inefficient cracking of the metalorganic sources. Photon enhancement below 260°C

did not significantly increase the growth rate and other methods of precracking (such as a cracker cell, hot filament) of the metalorganic sources may be needed to further extend the low temperature process window. We explored the effect (deposition rate, surface roughness) on the temperature (200–360°C) at a pressure of 1×10^{-6} Torr and found no enhancement which indicates that the absorption of TBP is temperature independent at 220 nm. As shown by Yoshimoto et al., precracking the PH_3 and photon enhancement with a nitrogen laser extended the growth of homoepitaxial GaP by CBE using TEG and PH_3 to 200°C, shown as a dashed line in Fig. 1 [14]. The presence of precracked phosphine fragments is thus essential for the enhancement of the growth rate under the conditions of light assisted CBE reported by Yoshimoto et al. [14]. However, an attempt at GaP growth on silicon at 200°C by laser induced MOCVD using TBP and TMG ($R_{V/III} = 8$) resulted in a polycrystalline film so that light assisted CBE may not be able to extend the process window to significantly lower temperature [15].

The results from SIMS and HRTEM reveal under the conditions of a rapid thermal annealing (900°C, 30 s) no interdiffusion of either gallium or phosphorus into the silicon substrate and therefore, with additional improvements in the quality the GaP film, may become useful as a dielectric for advanced silicon device processing.

5. Conclusion

The GaP films had excellent selectivity with regard to SiO_2 covered surfaces. Photon assistance did not increase the GaP growth rate below temperatures of 260°C due to the cracking of the TBP. A rapid thermal anneal at 900°C for 30 s of the Si/GaP/Si heterostructure reveals no significant interdiffusion of either phosphorus or gallium occurs.

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References

[1] M. Yoshimoto, K. Ozasa and H. Matsunami, J. Appl. Phys. 70 (1991) 5708.
[2] J.M. Olson, M.M. Al-Jassim, A. Kibbler and K.M. Jones, J. Cryst. Growth 77 (1986) 515.
[3] J.T. Kelliher, N. Dietz and K.J. Bachmann, in: Proc. 18th SOTAPOCS V93-27 (1993) 17.
[4] J.T. Kelliher, J. Thornton, N. Dietz, G. Lucovsky and K.J. Bachmann, Mater. Sci. Eng. B 22 (1993) 97.
[5] M. Yoshida, H. Watanabe and F. Uesugi, J. Electrochem. Soc. 132 (1985) 677.
[6] R. Lin, T.R. Gow, A.L. Backman, L.A. Cadwell, F. Lee and R.I. Masel, J. Vac. Sci. Technol. B 7 (1989) 725.
[7] C.H. Chen, C.A. Larsen, G.B. Stringfellow, D.W. Brown and A.J. Robertson, J. Cryst. Growth 77 (1986) 11.
[8] V.R. McCrary and V.M. Donnelly, J. Cryst. Growth 84 (1987) 253.
[9] H. Okabe, M.K. Emadi-Babaki and V.R. McCrary, J. Appl. Phys. 69 (1991) 1730.
[10] S.H. Li, N.I. Buchan, C.A. Larsen and G.B. Stringfellow, J. Cryst. Growth 96 (1989) 906.
[11] J.T. Kelliher and K.J. Bachmann, Mater. Res. Soc. Symp. 282 (1992) 51.
[12] J.T. Kelliher, J. Thornton, P.E. Russell and K.J. Bachmann, Mater. Res. Soc. Symp. 317 (1993) 597.
[13] Z. Lu, S. Habermehl, G. Lucovsky, N. Dietz, K.J. Bachmann and R.M. Osgood, Proc. 3rd Int. Symp. on Cleaning Technology in Semiconductor Device Manufacturing, New Orleans, 1993.
[14] M. Yoshimoto, A. Kajimoto and H. Matsunami, Thin Solid Films 225 (1993) 70.
[15] U. Sudarsan, T. Dosluoglu, N.W. Cody and R. Solanki, J. Cryst. Growth 94 (1989) 978.