GROWTH MECHANISM OF EPITAXIAL SILICON CARBIDE PRODUCED USING RAPID THERMAL CVD

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Abstract - A rapid thermal chemical vapour deposition system has been used for the growth of epitaxial silicon carbide layers on $\langle 111 \rangle$ and $\langle 100 \rangle$ silicon substrates. Silane/propane gas chemistry has been employed at growth temperatures less than 1000°C. The growth mechanism for SiC may be considered as carbonation of silane species adsorbed on the wafer surface. Sufficient propane is present in the gas ambient to allow complete carbonation, with the carbon concentration in the film saturating at 50%.

1. Introduction

Advanced silicon bipolar technology now employs polysilicon emitters, self aligned emitter-base structures and trench isolation techniques to reduce device size and increase operating efficiency. The subsequent reduction in parasitic capacitances has enabled the production of high performance circuits with gate delays below 30ps. The high emitter efficiency reported for polysilicon emitter devices allows base parameters to be optimised for high speed performance. However these polysilicon emitter devices normally depend on non-ideal interfacial oxide layers to block minority carrier injection and produce high gain.

The future production of high speed/high gain bipolar transistors will be based on the use of heterojunction structures. By using a wide bandgap semiconductor for the emitter it is possible to increase transistor gain, allowing base resistance to be minimised to give high speed operation. Silicon carbide (SiC) has attracted interest for use as a wide bandgap emitter material. The bandgap of beta-SiC is 2.2eV and it exhibits high thermal stability, controllable conductivity and high electron saturated drift velocity ($2.5 \times 10^7 \text{ cm s}^{-1}$) [1]. It is also reported that the conduction band offset with silicon is as low as 0.01eV, resulting in a valence band offset of over 1eV [2].

However the temperature needed for epitaxial growth of SiC on silicon can be as high as 1300°C. This is clearly unacceptable if the material is to be used as a replacement for polysilicon on a scaled device structure. Furumura et al [3] have produced epitaxial SiC on silicon at 1000°C using LPCVD, but with growth times of over 10 minutes. Although

they successfully produced heterojunction bipolar transistors, the emitter fabrication process would cause significant dopant redistribution in the narrow (100nm) base region of high performance transistors.

The approach presented in this paper is to combine rapid thermal processing (RTP) with low pressure CVD in a reduced thermal budget SiC deposition process at 970°C. Typically the deposition cycle lasts 1 minute and ramp up/down times are of the order of seconds. This paper begins by describing the rapid thermal processor used for the deposition experiments, and goes on to investigate the gas chemistry employed and the resultant deposition mechanism.

2. The Rapid Thermal CVD Equipment

The apparatus designed and constructed at Queen's University for rapid thermal CVD (RTCVD) is shown in diagrammatic cross-section in Fig.1. The single 2" process wafer is heated on both sides using tungsten-halogen lamps with a total power of 18kW. White ceramic reflector plates with a laser-quality glaze are employed as reflectors. The reaction chamber is a rectangular cross-section quartz tube which is evacuated using turbomolecular and rotary pumps. The chamber ultimate vacuum is around 5×10^{-7} mbar.

Fig. 1. Schematic cross-section of RTCVD equipment.

Six gas lines are at present available; 20% silane (in nitrogen), propane/methane, 0.1% phosphine (in nitrogen), nitrogen, hydrogen and tetrafluoromethane (CF_4). "Nanochem" point-of-use gas purifiers are installed in the SiH_4 , C_3H_8 and H_2 lines, thus reducing oxygen and water vapour levels in these gases to the low parts per billion (ppb) range. Such precautions have been shown to be necessary to achieve low temperature silicon epitaxy, and directly impact on SiC layer quality.

The maximum wafer temperature obtained in the system is 1063°C, with a maximum ramp rate of around 250°C/s. To achieve lower temperatures an analogue demand level (0-100%) is fed into a pulse-width modulator which produces a digital lamp control pulse of width (0-100ms) proportional to the analogue level. Solid-state relays are employed to control the lamps, thus avoiding the spurious electrical noise often associated with thyristor control circuits. For example, a 65% power setting results in the heating lamps being on for the first 65ms of each 100ms period, resulting in a wafer temperature of 970°C with negligible ripple. Wafer temperature had previously been calibrated against lamp power using a thermocouple in contact with the wafer surface.

In addition, the Queen's University RTCVD system (QUPLAS) incorporates an upstream microwave plasma generator operating at 2.45GHz. This facilitates room temperature in-situ wafer cleaning prior to beginning layer growth. The use of a CF₄ plasma preclean has been shown to promote epitaxial silicon growth at low temperatures [4].

3. Choice of Hydrocarbon Gas

The deposition of SiC requires both silicon and carbon bearing source gases. The QUPLAS reactor is a silane based system. However there are many hydrocarbon gases available which could be used as the carbon source and the correct choice will be critical in determining the composition of the resultant layers.

Initially methane (CH₄) was used as the carbon source gas. Silicon wafers were carbonised at 970°C at a pressure of 1mbar with a methane flow of 50sccm. ERDA revealed that a 15 minute process yielded a carbonised substrate containing 5.2% carbon to a depth of 74nm. Although the methane decomposed at 970°C, when a silane/methane gas ambient was employed to attempt SiC deposition, a silicon layer containing less than 1% carbon was deposited, as revealed by ERDA. It is presumed that the adsorption of silane on the silicon surface is stronger than that for methane and hence the decomposition of methane is retarded. Hence a more reactive hydrocarbon is required.

Methane is composed of four C-H sigma bonds, and requires an energy of 4.14eV to break into the reactive methyl radical (CH₃). Also, the bond distance is only 0.109nm, showing that methane is a compact, strongly bound molecule. Propane (C₃H₈), however, has two C-C sigma bonds with a bonding energy of 3.47eV and a bond distance of 0.154nm, in addition to the eight C-H bonds similar to those in methane. Hence the decomposition of propane is relatively favourable and occurs by the breakup of C-C bonds,

Hence the propane breaks into a methyl and an ethyl radical (CH₃CH₂), which are each highly reactive, and are capable of reaction with silane adspecies. An even more reactive hydrocarbon for combination with silane may be acetylene (C₂H₂). This gas has a carbon to carbon triple bond which may undergo "addition" reactions during which silane radicals could be inserted into the molecule across the carbon bond. As a sufficiently pure source

of this gas has not yet been located, the SiC deposition experiments were thereafter restricted to silane/propane chemistry.

4. Layer Deposition and Characterisation

Stoichiometric layers of SiC were deposited by Limited Reaction Processing (LRP) at 970°C using silane/propane gas chemistry. In the LRP mode of operation the gas flowrates are established before the process wafer is rapidly ramped up to temperature. The growth process is therefore thermally triggered and continues for the time during which power is applied to the heating lamps. Process pressures over the range 0.3 to 10mbar were investigated, and the effect of varying the silane/propane flowrate ratio over the range 0.01 to 0.2 was examined. Fig. 2 is a typical SIMS depth profile for a SiC layer deposited at 970°C at a pressure of 10mbar and with $\text{SiH}_4/\text{C}_3\text{H}_8=0.01$. Also shown is a SIMS profile of a stoichiometric single-crystal standard, providing evidence of the composition of the RTCVD deposited material. Analysis using XPS revealed that there was a high degree of Si-C bonding in the layer.

Fig. 2. SIMS profiles of SiC standard and LRP-deposited material.

4.1 Growth Mechanism

Fig. 3 shows carbon concentration and incorporation rate as a function of $\text{SiH}_4/\text{C}_3\text{H}_8$ flowrate ratio, as determined by SIMS. Incorporation rate is the product of concentration and deposition rate and gives a measure of the quantity of an element included in a depositing layer in unit time.

As the silane flowrate was increased from that required for stoichiometric growth ($\text{SiH}_4/\text{C}_3\text{H}_8=0.01$) the carbon concentration in the layer decreased. However the

incorporation rate of carbon actually increased. This may be explained by the layer growth mechanism of rapid carbonation of silane adspecies. As the proportion of silane in the ambient is increased then more silane species will be adsorbed onto the hot wafer surface. There is sufficient propane in the ambient to provide enough carbon species to react with (carbonise) the depositing silicon, hence increasing the carbon incorporation rate. However the formation of Si-Si bonds outpaces the carbonation process and so stoichiometry is lost. A consequence of this growth mechanism is that it is not possible to grow a layer containing more than 50% carbon.

Fig. 3. Carbon concentration and incorporation rate versus flowrate ratio.

This carbon saturation theory was verified when SIMS measurements were made of carbon concentration over the pressure range 0.3 to 10mbar (Fig. 4). There appears to be a critical pressure of 2mbar, above which the carbon concentration is 50%, and below which non-stoichiometric SiCARB films are produced.

Fig. 4. Carbon concentration versus pressure.

4.2 Minimisation of Oxygen Contamination

Initial layers produced at 970°C and 10mbar without process gas purification showed oxygen levels around $6 \times 10^{20} \text{cm}^{-3}$ or 0.6% of the film. The addition of the Nanochem purifiers was successful in reducing this contamination level to around 10^{19}cm^{-3} or 0.01% of the film. At this stage reference was made to the work of Ghidini and Smith [5] on epitaxial silicon films. They established that there existed critical partial pressures of oxygen and water vapour below which stable oxides would not be included in a growing silicon film. This implies that a reduction in process pressure at a given temperature could result in a dramatic decrease in oxygen concentration as the critical pressure is passed.

Fig. 5 shows the oxygen concentrations in SiC films deposited at pressures in the range 0.3 to 10mbar. It is clear that oxygen levels in the films decreased as the process pressure was reduced, reaching $6 \times 10^{17} \text{cm}^{-3}$ at 0.3mbar. However, as has already been noted, layers deposited at this pressure are not stoichiometric SiC.

Fig. 5. Oxygen concentration versus pressure.

Another important process variable is the speed at which the process gases are pumped through the reaction chamber. The pump speed in the QUPLAS reactor was as low as 0.175l/s at 10mbar where the pump was severely throttled, rising to 5.83l/s at 0.3mbar with no restriction in the pumping line. As pressures greater than 2mbar must be achieved for stoichiometric layer growth, chamber pressure was increased by increasing process gas flowrates rather than by pump throttling. In this way rotary pump speed is maintained and SiC layers were deposited at 7.8mbar with an oxygen concentration of $2 \times 10^{18} \text{cm}^{-3}$. Faster pump speeds will be used following the installation of an Edwards roots/rotary combination.

However SIMS analysis of the SiCARB layers produced at 0.3mbar revealed that the interfacial oxide had been removed much more successfully than in higher pressure processes, even though the CF_4 plasma clean had been employed in all cases. It is

assumed that a loosely bound oxide reforms on the wafer surface in the period between the plasma clean and layer deposition. This oxide is readily desorbed during the temperature ramp-up at low pressure where deposition rate is slow. At higher pressures the deposition rate of the layer is so fast that the oxide does not have time to desorb and so is trapped at the interface.

4.3 Two-stage Process for Epitaxial SiC Growth

As a result of the foregoing investigations it is clear that an initial 30s growth period at 0.3mbar, followed by bulk layer growth at 5mbar would produce a stoichiometric SiC layer with no oxide interface to the silicon substrate. A SIMS profile of such a layer is shown in Fig. 6, the total process time being only 50s.

Fig. 6. SIMS profile of SiC deposited using dual pressure process.

As the interfacial oxide has been successfully removed, the conditions for epitaxial alignment with the substrate are more likely to be met. Fig. 7 shows an electron diffraction pattern for such a SiC layer grown on a $\langle 111 \rangle$ silicon substrate. Along with the pattern of spots expected for a $\langle 111 \rangle$ -oriented layer, "forbidden" spots are also observed. These are indicative of an aligned layer containing a significant number of crystal lattice defects. This is not unexpected as there is a considerable 20% lattice mismatch between SiC and silicon. Epitaxial alignment has also been observed on $\langle 100 \rangle$ silicon substrates.

Fig. 7. Electron diffraction pattern of SiC grown on $\langle 111 \rangle$ silicon.

5. Conclusions

Silane/propane gas chemistry has been employed in the production of epitaxially aligned SiC layers at 970°C using rapid thermal CVD. A growth mechanism comprising carbonation of silane adspecies has been deduced. Process pressures greater than 2mbar are required for stoichiometric layer growth, but oxide interface desorption requires a low pressure of 0.3mbar. A dual pressure process has been devised which facilitates epitaxial alignment of silicon carbide to both $\langle 111 \rangle$ and $\langle 100 \rangle$ silicon substrates.

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