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Growth and characterization of nitrogen-doped polycrystalline 3C-SiC thin films for harsh environment MEMS applications

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Abstract
Polycrystalline 3C-SiC films, \textit{in situ} doped with nitrogen, are grown by low-pressure chemical vapor deposition (LPCVD) on 100 mm Si (1 0 0) wafers at 800 °C using methylsilane and ammonia precursors. The effects of \(\text{NH}_3\) and dichlorosilane precursor, as an additional silicon source, on material properties such resistivity, residual stress, strain, strain gradient as well as crystallinity and surface morphology are investigated. By varying these parameters, the electrical and mechanical properties of the films are optimized for MEMS applications. Films with a resistivity of 0.026 ± 0.001 Ω cm, residual stress of 254 ± 16 MPa and strain of 4.5 \times 10^{-4}, corresponding to the biaxial modulus of 564 GPa, and strain gradient of 5.8 \times 10^{-4} \mu m^{-1} are achieved.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Recent developments in such industries as automotive, petroleum and aerospace require stable, high-temperature materials for solid-state sensors and electronics [1, 2]. Silicon carbide, a wide band gap semiconductor with superior mechanical strength, chemical inertness and high thermal conductivity, is suitable for such applications and more broadly for microelectromechanical systems (MEMS) in harsh environments [3, 4].

Compared to 4\(H\) and 6\(H\) hexagonal SiC, the 3C cubic SiC films can be grown heteroepitaxially on a variety of substrates at a reduced temperature [5] and hence enable more process freedom, especially for surface micromachining. In order to deposit 3C-SiC films at low temperatures, organosilicon precursors having an alternate Si–C bonding structure have been attempted. Examples include dimethylisopropylsilane \((\text{CH}_3)_2\text{CHSiH(CH}_3)_2\), methyltrichlorosilane \((\text{CH}_3\text{SiCl}_3\)), 1,3-disilabutane \((\text{CH}_3\text{SiH}_2\text{CH}_2\text{SiH}_3\)) and methylsilane \((\text{H}_3\text{SiCH}_3\)) [6–9]. Methylsilane is an attractive precursor as it is available in the high-purity large-scale form. Studies have demonstrated the growth of undoped polycrystalline 3C-SiC (poly-SiC) using methylsilane (MS) at temperatures as low as 750 °C [10]. Using this precursor, the n-type doping has been reported using \(\text{N}_2\) and \(\text{NH}_3\) as the dopant precursors at temperatures above 1000 °C [11]. Compared with \(\text{N}_2\), ammonia enables SiC doping at lower temperatures, benefiting from its lower dissociation energy. Thus, the n-type doped SiC film deposition process using MS and \(\text{NH}_3\) allows the deposition of doped 3C-SiC films at lower deposition temperatures.

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The dopant incorporation into the SiC lattice is known to affect the crystallinity, morphology and mechanical properties of the films [12–14]. In particular for MEMS devices, such properties as resistivity, residual stress and strain gradient through the film thickness as well as crystalline structure can greatly impact the device performance. In order to realize the poly-SiC as the structural layer in MEMS, the electrical, mechanical and structural properties of the film must be controlled simultaneously, yielding conductive films with moderate stress, low strain gradient and high crystallinity. In this paper, material properties such as resistivity, residual stress, strain and strain gradient as well as crystallinity and surface morphology are characterized for n-type poly-SiC deposited by LPCVD using MS and ammonia precursors. In particular, the effects of ammonia and dichlorosilane (DCS) flow rates on these properties are investigated and qualitatively explained. Finally, by optimizing the growth parameters, doped polySiC films suitable for many MEMS applications are demonstrated.

2. Experimental details

2.1. Deposition details

To ensure electrical isolation for sheet-resistance measurements, Si (100) substrates are isolated with a layer of thermally grown SiO2, with an approximate thickness of 0.5 μm. Prior to deposition, wafers are immersed for 10 min in a piranha solution (85% sulfuric acid and 17% hydrogen peroxide at 120 °C), rinsed in deionized water (18 MΩ cm) and N2 dried. The final resistivity of the rinsing water is greater than 16 MΩ cm. The wafers are loaded in a borosilicate glass boat (Angle Slotted Quartz, Inc.) which can hold up to 15 wafers with an inter-wafer spacing of 1.2 cm. The boat, referred to as closed boat [15], consists of a cylinder which surrounds completely the wafers with slits on its side to allow reactant gases to reach the wafers. The boat, thus prepared, is loaded in a commercial LPCVD Tystar Titan II furnace with a 90 cm hot-zone region set at 800 °C. Deposition pressure is set at 170 mTorr with an Edwards QMB500 roots blower in conjunction with an Edwards QDP40 mechanical pump. Silicon carbide films are deposited using methylsilane (Voltaix, Inc., 99.98% purity) as the precursor and H2 (Praxair, Inc., 99.99% purity) as the dilution gas. The MS and H2 flow rates are set at 30 sccm and 240 sccm, respectively, since these parameters yielded undoped polycrystalline 3C-SiC film with the lowest stress and strain gradient values [16]. Dichlorosilane (Praxair, Inc., 99.99% purity) is employed as the additional silicon source to control the film stress and resistivity with its flow rate ranging from 0 to 6 sccm. NH3 (Praxair, Inc., 99.99% purity) is used as the dopant gas with its flow rate adjusted in the range of 0–6 sccm. The deposition rates are found to have weak dependence on the DCS and NH3 flow rates (~0.5 ± 0.1 μm h−1). The highest film deposition rate is achieved for the DCS and NH3 flow rates of 6 sccm and 3 sccm, respectively, while the lowest film deposition rate occurs when the DCS and NH3 flow rates are 3 sccm and 3 sccm, respectively. The deposition time for SiC LPCVD is controlled based on the film growth rate at different process parameters, such that the thickness of the SiC films is around 300 nm for all experiments reported in this work. This is to enable a more consistent comparison between the films deposited under different conditions, without the convoluted effect of variations in film thickness. The film stress and resistivity (described in the following section) are averaged values based on measurements made on three wafers occupying the same three equally spaced positions of the boat in each run.

2.2. Characterization techniques

Grazing incidence x-ray diffraction (Philips 1830 PW) is employed to investigate the crystal orientation of the films. Surface morphology is analyzed with atomic force microscopy (AFM) operating in contact mode (Digital Instruments Multimode Nanoscope IIIa). Room-temperature sheet resistance is obtained using a four-point probe station (Signatone). Optical reflectometry with a thickness measurement system (NanoSpec model 3000) is employed to determine film thicknesses. For each wafer, measurements are taken at five positions, the center of the wafer, 1 cm radially inward from the primary flat and 1 cm radially inward from the edge of the wafer at 90° intervals from the primary flat. Average residual film stress is determined using the Tencor FLX-2320 system. Film strain and strain gradient are determined by the microfabricated strain gauge and cantilever beam array [15].

3. Results and discussion

As reported previously [16], the undoped SiC film strain gradient reaches the lowest value at a DCS flow rate of 30 sccm for a methylysilane flow rate of 3 sccm; thus, to study the effect of NH3 flow rate fraction on film stress and resistivity variations, the DCS flow rate is fixed at 3 sccm. Figure 1 displays the effect of NH3 flow rate on the resistivity and residual stress of the SiC films deposited with the DCS flow rate of 3 sccm. With an increase in NH3 flow rate, the resistivity drops initially by several orders of magnitude and then plateaus, reaching the value of 0.016 ± 0.001 Ω cm at a 4 sccm NH3 flow rate. In parallel, residual stress is tensile and increases with NH3 flow rate, reaching 953 ± 16 MPa at a 4 sccm NH3 flow rate.

The effect of NH3 flow rate on SiC film stress may be due to variations in a lattice constant. It is known that intrinsic stress of a film is affected by chemical composition variations [21]. In particular, the elongation of the lattice spacing leads to more compressive stress or less tensile stress, while the shrinkage of the lattice spacing causes more tensile stress or less compressive stress. The incorporation of nitrogen in the SiC lattice results in a reduction of the lattice constant due to a smaller covalent radius of N than that of C or Si. A theoretical model of doping-induced lattice reduction has been presented for homoepitaxial 4H-SiC [17]. According to the authors, as the doping level reaches the 1019 cm−3 range, the reduction in the lattice constant, Δa, with respect to the lattice constant of the undoped film, a0, falls in the range of
Δa/a₀ ∼ 10⁻⁴. A similar lattice shrinkage has been experimentally reported for polycrystalline 3C-SiC film upon nitrogen doping [18]. The authors reported the lattice compression of about 3 × 10⁻³ for the films with a carrier concentration of 6.8 × 10¹⁷ cm⁻³. In our experiments, when the DCS flow rate is fixed at 3 sccm, the SiC (1 1 1) peak, the main peak in the XRD spectra, shifts to higher 2θ values with increasing NH₃ flow rate (figure 2), reaching a value of 0.1° at a NH₃ flow rate of 3 sccm. This value corresponds to the lattice shrinkage of ∼2 × 10⁻³ compared to the undoped film. The shrinkage of crystalline lattice with doping level may be responsible for the increase in the tensile stress within the deposited film, as reported in figure 1.

To study the effect of DCS addition on film stress and resistivity, the NH₃ flow rate is fixed at 3 sccm and the DCS flow rate is changed from 0 to 6 sccm. It is reported that SiC film stress can be controlled by adding DCS to the reaction gases [16]. For the undoped films deposited at 800 °C and 0.17 Torr, the film stress is found to decrease by DCS addition to the lowest point of 196 ± 19 MPa, at 3 sccm DCS, and then increase when DCS flow rate is further increased. For the doped films, the residual stress decreases monotonically from 1414 ± 20 MPa to 339 ± 11 MPa within the examined range of DCS flow rate, as shown in figure 3. In parallel, the resistivity decreases from 0.595 ± 0.010 Ω cm to 0.011 ± 0.001 Ω cm and plateaus around the DCS flow rate of 3 sccm.

The influence of the silicon source on the nitrogen incorporation in SiC film may be explained by site competition between nitrogen and carbon for C sites [19]. Nitrogen can occupy either the Si or C site, with the latter site being more energetically favorable. Analogously, the increase in Si component in the SiC lattice, due to DCS addition, results in higher atomic nitrogen incorporation, thus lowering film resistivity. The increase in Si component also leads to longer average bond length since Si atomic radius is larger than those of C and N and thus the decrease in tensile stress in the film (figure 3).

For MEMS applications, high residual stress can cause the microstructure to buckle if compressive or crack if tensile. The strain gradient of the film leads to the curvature of the released structures such as cantilevers. Thus, it is important to control both of them. The residual strain gradient is the result of the variation in stress through the film thickness. Cantilevers with negative strain gradient bend down resulting from the compressive strain or less tensile strain near the film surface, while cantilevers with positive strain gradient bend up due to the increase of tensile strain with film thickness. In this paper, the strain gradients of the films with residual stress lower than 500 MPa (figures 1 and 2) are examined. Table 1 shows that the lowest strain gradient of 5.8 × 10⁻⁴ μm⁻¹ is obtained with 3 sccm DCS and 1.5 sccm NH₃. Although DCS addition in the reaction gases can reduce both the film stress and resistivity, a further increase in the DCS flow rate to more than 3 sccm leads to large positive strain gradient.

For poly-SiC as the structural materials for many MEMS applications [1], the optimized film deposition parameters are films with low resistivity, stress and strain gradients. As such, the most optimum films are those deposited with 3 sccm DCS and 1.5 sccm NH₃, while maintaining the deposition temperature at 800 °C and pressure at 0.17 Torr with 30 sccm MS and 240 sccm H₂ flow rates. Under these deposition conditions, the film strain gradient examined by microfabricated strain gauge is 4.5 × 10⁻⁴. Thus, the biaxial modulus E/(1 − γ) of the films, where E is Young’s modulus of the films, is 564 ± 35 GPa. If we assume Poisson’s ratio (λ) of polycrystalline 3C-SiC to be 0.21 [20], Young’s modulus of the film is calculated to be 445 ± 28 GPa.

Since the crystalline structure of the film is important for dynamic MEMS devices, such as microresonators and filters, the crystalline structures of the undoped and doped films with the optimized mechanical and electrical properties are investigated next. As shown in figure 3, the 3C-SiC...
Table 1. Strain gradient versus gas flow rates for deposition at 800 °C and 0.17 Torr with 30 sccm MS and 240 sccm H2.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>DCS = 6 sccm</th>
<th>DCS = 3 sccm</th>
<th>DCS = 3 sccm</th>
<th>DCS = 3 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3 = 3 sccm</td>
<td>2.5 \times 10^{-3}</td>
<td>1.2 \times 10^{-3}</td>
<td>5.8 \times 10^{-4}</td>
<td>-5.2 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Figure 3. Resistivity and residual stress dependences of the poly-SiC films on DCS flow rate. Other growth parameters are 3 sccm NH3, 30 sccm MS and 240 sccm H2 flow rates; deposition temperature of 800 °C and pressure of 0.17 Torr.

Figure 4. AFM images (2 \times 2 \mu m^2 and 150 nm z-scale) of \sim 300 nm thick SiC films, (a) undoped film (b) doped film using 1.5 sccm NH3. Films are deposited at 800 °C and 0.17 Torr with 3 sccm DCS, 30 sccm MS and 240 sccm H2.

(111), 3C-SiC (220) and 3C-SiC (311) peaks are observed, indicating the polycrystalline nature of the films. The XRD data clearly show the sharper and more intense 3C-SiC peaks for doped films, indicating enhancement in crystallinity and larger grain size of the films deposited with 3 sccm DCS and 1.5 sccm NH3 flow rates with respect to undoped films. The AFM plane-view images taken for the undoped film and the film deposited with 3 sccm DCS and 1.5 sccm NH3 gases are shown in figure 4. The films show a granular island-like surface morphology, commonly observed in films deposited by low-pressure chemical vapor deposition. The increased grain size, as suggested by XRD, may be responsible for the increased surface roughness and surface-projected grain size of the doped film.

Hasegawa et al proposed that the reduction in C–C bonds leads to an increase in XRD SiC (111) intensity and in the grain size [12]. The model is based on the assumption that incorporation of N atoms may act to exclude excess C atoms forming C–C bonds, which exist in regions surrounding the SiC grains, and thus enhance the formation of a more crystalline Si–C network. In fact, an enhancement in crystallinity has been reported at moderate N-doping concentration in poly-3C films deposited by 1,3-disilabutane [4,18]. Our results are consistent with these earlier findings.

4. Conclusion

Polycrystalline 3C-SiC films, in situ doped with nitrogen, are grown on Si (100) wafers by LPCVD at 800 °C using methylsilane and ammonia. The dependences of electrical and mechanical properties on NH3 and DCS flow rate are investigated. The incorporated nitrogen causes a compression of the SiC lattice, thus increasing the tensile stress in the films. It is suggested that nitrogen competes with carbon for the C sites in the SiC lattice when extra silicon source is available, leading to the observed reduction in film resistivity upon DCS addition. The additional silicon source also helps to reduce the film stress due to the larger atomic radius of Si. A reduction in C–C bonds in the grain boundary by doping may be responsible for the observed enhancement in film crystallinity upon doping. The film that appears most suitable for MEMS applications has a resistivity of 0.026 \Omega \, cm, residual stress of 254 MPa and strain of 3.5 \times 10^{-5} with a strain gradient of 5.8 \times 10^{-4} \mu m^{-1}. Post-deposition treatments to further reduce SiC film stress are being investigated.

Acknowledgments

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