Electrical, mechanical and metal contact properties of polycrystalline 3C-SiC films for MEMS in harsh environments

Jingchun Zhang a, Carlo Carraro a, Roger T. Howe b, Roya Maboudian a,*

a Department of Chemical Engineering, University of California, Berkeley, California 94720, USA
b Department of Electrical Engineering, Stanford University, Stanford, California 94305, USA

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Abstract

Polycrystalline 3C-SiC (poly-SiC) is a promising structural material for microelectromechanical systems (MEMS) used in harsh environments. In order to realize poly-SiC based MEMS devices, the electrical, mechanical and metal contact properties of poly-SiC have to be optimized. The poly-SiC films, reviewed here, are deposited by low pressure chemical vapor deposition using 1,3-disilabutane (DSB) as the single precursor, and are in-situ doped using NH3 (n-type) and trimethylaluminum (p-type). The effects of doping on film structure, resistivity, residual stress and strain gradient have been examined. A bi-layer deposition scheme is developed to minimize the strain gradient without compromising the electrical resistivity of film. The temperature coefficient of resistivity (TCR) is also characterized and is found to be negative over 304–638 K. Ohmic nickel and platinum contacts to n-type doped poly-SiC are obtained and characterized. A stable metal contact up to 300 °C in air is demonstrated.

Keywords: SiC; MEMS; Electrical properties; Mechanical properties; Metal contact

1. Introduction

Microelectromechanical systems are miniature integrated systems including both mechanical and electronic components [1]. Through the batch fabrication techniques similar to those used for integrated circuits, a variety of MEMS sensors and actuators have been manufactured with high reliability at relatively low cost. The development of MEMS technology since 1980s is based on the well-developed Si-based integrated circuits technology. Recently, for applications in such industries as automotive, petroleum and aerospace, there are increasing demands for MEMS devices that can operate in harsh environments, including high temperatures and severe mechanical and chemical conditions. However, the applications of Si-based MEMS in harsh environments are limited due to the inherent physicochemical properties of Si. Silicon carbide [2] (SiC) is a wide band gap semiconductor, with superior mechanical and chemical properties such as high Young’s modulus, hardness and resistance to corrosion and oxidation, and hence, it promises to be an attractive substitute for Si as a structural material for MEMS in harsh environments [3].

Current research trends indicate a growing interest in the use of polycrystalline cubic 3C-SiC (poly-SiC) as a MEMS structural material [4], since it can be deposited on a variety of substrate materials and hence, enables more process freedom, especially for surface micromachining. Recent research has demonstrated the growth of poly-SiC thin film utilizing single precursor low-pressure chemical vapor deposition (LPCVD) at relatively low temperatures (800 °C) [5]. A low temperature line-of-sight deposition of amorphous SiC with an ion beam sputter deposition technique has also been developed for the encapsulation of released SiC MEMS devices [6]. In order to realize poly-SiC based MEMS devices, various materials properties such as resistivity, residual strain, and strain gradient have to be optimized. In this review, we present our recent results on the characterization of electrical, mechanical and metal contact properties of poly-SiC films. Although individual materials property (e.g., strain gradient) can be controlled by process conditions, the simultaneous optimization of other properties (e.g., resistivity) is usually challenging. Here, we also present an approach we have developed to enable optimization of the various MEMS-relevant properties.
2. Deposition and in-situ doping of poly-SiC

Poly-SiC films are deposited using horizontally oriented hot-wall tubular low-pressure chemical vapor deposition reactors (LPCVD), with a base pressure of approximately 10⁻⁶ Torr by a turbomolecular pump. The precursor used is 1,3-disilabutane (DSB), SiH₂–CH₂–SiH₂–CH₃, as a single precursor. The DSB (Gelest Inc., >95% purity) is further purified by freeze-pump-thaw cycles using liquid N₂. The substrates are bare Si(100), and SiO₂-coated Si(100) dies which are prepared by thermally growing a SiO₂ layer (100 to 500 nm) on Si(100) wafers. The SiO₂ layer is used to electrically isolate the deposited film for electrical characterization and for MEMS device fabrication.

For n-type films, gaseous NH₃ (Matheson, 5% NH₃ in H₂) is used as the precursor for nitrogen. The reactor (TekVac CVD-300-M) consists of a 600 mm long quartz tube with a 75 mm inner diameter. Mass flow controllers are used to manipulate the flow rates of the precursor gases. The NH₃/DSB flow rate ratio is varied ranging from 0 to 5:100 (referred to as 0 to 5% nitrogen doped) with the DSB flow rate typically kept at 5 sccm. The deposition temperature is 800 °C. The typical deposition time is 30 min yielding a film thickness of about 1 μm.

For p-type films, gaseous trimethylaluminum (TMA) is used as the aluminum precursor. The p-type aluminum doped films are deposited in a custom-made reactor, which consists of an alumina tube (15 mm inner diameter, 150 mm long) with a 50 mm long hot-wall zone, a sample stage with an integrated thermocouple, and variable leak valves for the introduction of the precursor gases. DSB is first introduced to the reactor to reach a process pressure of 100 mTorr. Then the DSB flow rate is kept constant and TMA is introduced. The ratio of TMA/DSB is monitored by the total process pressure, which ranges from 100 to 110 mTorr corresponding to TMA/DSB ratios from 0 to 10:100 (referred to as 0 to 10% aluminum doped). The deposition temperature is 850 °C. The typical deposition time is 30 min yielding a film thickness of about 2 μm.

3. Effect of doping on film crystalline structure and resistivity

Proper and controllable electrical resistivity is one of the most critical material properties for MEMS applications. Generally, a low resistivity is desired to reduce the energy dissipation, and enhance the system energy transfer performance, which is extremely important in MEMS transducers [7]. As a semiconductor, the electrical resistivity of SiC can be changed by intentional impurity doping. Doping of single crystalline SiC has been extensively studied and documented [8]. However, the dopant incorporation and carrier transport mechanism in polycrystalline semiconductors, such as poly-Si, may differ from those of their single crystalline counterparts [9]. For 3C-SiC, nitrogen is known to be a good n-type dopant which forms a shallow donor level (54 meV) [10]. Nitrogen is usually present in SiC even without intentional doping from the residual nitrogen gas in the deposition system and precursors, which makes the undoped SiC often lightly n-type doped [2]. Aluminum is usually employed as a p-type dopant, but it has a high ionization energy (257 meV) [11]. Typically, doping can be performed either in-situ during the growth process by adding the dopant precursor, or after the crystal growth by ion implantation and diffusion. We have examined the in-situ doping process due to its simpler process and the avoidance of high temperature post-annealing. The effect of doping on the film crystalline structure and resistivity is reviewed next [12].

3.1. Nitrogen doped poly-SiC

The nitrogen doped poly-SiC films deposited at 800 °C are found to exhibit a strong (111) texture according to the X-ray diffraction (XRD) spectra. In the absence of epitaxy between the film and the substrate, the preferred growth orientation has been explained by the evolutionary selection rule, which states that the faster growing crystallographic plane envelopes the other planes and thus determines the final orientation [13]. The SiC (111) XRD peak shape shows dependence on the NH₃/DSB flow rate ratio, as shown in Fig. 1. With the increase in nitrogen content, the SiC(111) peak position shifts to higher 2θ values, which corresponds to a decrease in 3C-SiC lattice constant. The peak position of undoped poly-SiC corresponds to a lattice constant of 4.360 Å, which agrees well with that of single crystalline 3C-SiC (4.3596 Å [8]). The increase in nitrogen content results in a reduction in the lattice constant to 4.352 Å for 4% doped sample. The smaller covalent radius of N (0.70 Å) than that of C (0.77 Å) and Si (1.17 Å), the substitutional incorporation of nitrogen into SiC results in the shrinkage of SiC lattice. Hasegawa and coworkers have reported a SiC lattice shrinkage to 4.33 Å by nitrogen doping in a plasma enhanced poly-SiC deposition process [14]. The small lattice variation in our doping process indicates that the N atom incorporation into SiC crystalline lattice is very limited.
even in the highest NH$_3$/DSB ratio. With the increase in doping, the intensity of the XRD peak decreases measurably which indicates a decrease in the overall degree of crystallinity. Meanwhile, the peak broadens significantly, which corresponds to smaller grain size. The presence of a shoulder in the XRD spectra at higher 2$\theta$ indicates regions with smaller lattice constant (higher nitrogen incorporation), which may be related to the formation of nitrogen-vacancy complex [15], even in the undoped samples due to unintentional nitrogen doping. The nitrogen concentration in the undoped SiC is less than 0.01 at.% according to the secondary ion mass spectrometry analysis (SIMS). The low nitrogen concentration is not expected to affect the mechanical properties of SiC film, but it appears to affect the p-type doping.

Fig. 2 shows the resistivity of the nitrogen doped poly-SiC films as a function of NH$_3$ to DSB flow rates ratios. With the increase in NH$_3$/DSB ratio, the resistivity initially drops over several order of magnitude, and then, more gradually reaches a value of $\sim$0.03 $\Omega$ cm. The carrier concentration, obtained by Hall-probe measurements, and the nitrogen concentration, obtained by SIMS both increase with doping as displayed in Fig. 3. However, with the increase in nitrogen doping, the SiC crystallinity decreases and the fraction of amorphous grain boundaries increases, which has an inverse impact on resistivity. The combination of these two trends resulted in the plateau observed in the resistivity data. The nitrogen concentration is about three orders of magnitudes higher than carrier concentration. This implies that most of the nitrogen atoms are not activated. The inactive nitrogen atoms may have incorporated into the amorphous grain boundaries as well as forming the nitrogen complex as indicated by the shoulder peak in XRD spectra.

### 3.2. Aluminum doped poly-SiC

The aluminum doped poly-SiC films are found to exhibit a strong SiC(111) texture with weak SiC(220) orientation. The variation of SiC(111) peak with aluminum doping is shown in Fig. 4. In contrast to nitrogen doping, aluminum doping makes the (111) peak position down-shifted to lower 2$\theta$ value, which corresponds to an expansion of SiC lattice. Because of the larger atomic size of aluminum (1.26 Å), the incorporation of aluminum is expected to expand the SiC lattice. The peak

![Fig. 2. Resistivity of nitrogen doped poly-SiC films as a function of NH$_3$/DSB flow rate ratio at the deposition temperature of 800 °C.](image1)

![Fig. 3. Nitrogen and carrier concentrations in the nitrogen doped poly-SiC films as a function of NH$_3$/DSB flow rate ratio at the deposition temperature of 800 °C.](image2)

![Fig. 4. SiC(111) XRD peak of Al doped poly-SiC films as a function of TMA/DSB pressure ratio at the deposition temperature of 850 °C.](image3)
intensity also varies with aluminum doping. But unlike the monotonic effect of nitrogen doping, aluminum doping first increases the peak density and then decreases it. The positive effect of TMA on SiC crystallization has been observed by reducing the deposition temperature of single crystalline SiC [16]. However, excess TMA degrades the crystal quality. The shoulder peak feature is still present in aluminum doped films, and is attributed to the nitrogen-vacancy complex due to the residual nitrogen in the deposition system.

With the increase in TMA content, the film resistivity first increases, then decreases to around 16 Ω cm. The initial increase in resistivity most likely stems from the compensation of p-type impurity with the n-type impurity which arises from the residual nitrogen in the reactor. Due to the high ionization energy of p-type dopant, higher resistivity is expected for p-type SiC films than that of n-type ones, as is observed in our system.

3.3. Effect of temperature on film resistivity

Nitrogen doped poly-SiC films appeared the optimum for MEMS application, due to their low film resistivity. Thus, the nitrogen doped films were further studied for the temperature effect on resistivity. Fig. 5 shows the effect of temperature on the resistivity of 0, 1 and 5% nitrogen doped poly-SiC films from 304 to 638 K. In this temperature range, the resistivity for all the samples decreases with increasing temperature. The 5% doped poly-SiC film displays about 35% linear resistivity drop, while the resistivity of undoped poly-SiC drops by two orders of magnitude over the temperature range studied.

The temperature effect on resistivity is usually described by the temperature coefficient of resistivity (TCR), which is defined as the fractional change in resistivity per unit change in temperature at a specified temperature. As shown in Fig. 6, TCR of 5% doped poly-SiC has the least temperature dependence, with a value of −0.17 to −0.10% K⁻¹. TCR of undoped poly-SiC changes from −2.4 to −1.3% K⁻¹ with an increase in temperature. The TCR dependence on film resistivity is similar to that of poly-Si, and the TCR values for poly-SiC with similar resistivities closely match those for poly-Si [17].

The negative TCR is caused by the energy barrier at the grain boundaries due to the capture of carriers by the dangling bonds and defects within the grain boundaries. The capture of electrons at the grain boundaries results in a non-uniform charge distribution, which is negative inside grain boundaries and positive outside grain boundaries. According to Poisson’s equation, such charge distribution corresponds to an energy band structure with a potential energy barrier (Vₜₚ) at grain boundaries. With an increase in temperature, the transport of carriers through the barrier by thermionic emission is enhanced, leading to a decrease in the resistivity, or a negative TCR. According to a one-dimensional model [9], the temperature dependence of resistivity may be expressed as:

$$\rho \propto T^{-1/2} \exp \left( \frac{qV_{t}}{k_{B}T} \right)$$

where $k_{B}$ is the Boltzmann constant. Our resistivity vs. temperature data are fitted to this model and the results are plotted in Fig. 5. The extracted energy barrier height is 0.29, 0.0745 and 0.0402 eV for 0, 1 and 5% doped films respectively. Due to the impedance of the energy barrier to carrier transport, the barrier height variation also contributes to the room temperature resistivity variation with nitrogen doping.

4. Doping effect on residual strain

Residual strains including average strain and strain gradient through the thickness of the film are among the most important film properties, especially for surface micromachined MEMS devices, which are typically constructed by constrained and cantilevered structures. Through specific device design (e.g., folded-suspension), excess average residual strain can be
relieved in some situations [18]. However, the depression of strain gradient in films remains challenging.

The effect of nitrogen doping on the average strain and strain gradient has been characterized by microfabricated strain gauges and cantilever beam arrays (CAB) [19]. The nitrogen doped poly-SiC films have positive (tensile) average strains which increase with nitrogen doping, ranging from 0.10% to 0.21%. The strain gradients of all films are negative with values ranging from $-2 \times 10^{-4}$ to $-5 \times 10^{-5} \mu$m$^{-1}$. This negative strain gradient is too large for many MEMS designs.

For poly-SiC films with tensile strain, negative strain gradient is usually observed [20,21]. The development of the strain gradient is related to the variation in microstructure through the film thickness, as reported in a recent transmission electron microscopy (TEM) study on poly-SiC films [22]. The strain gradient of poly-SiC films can be controlled by film deposition conditions, such as deposition temperature and precursor flow rates. With the increase in the deposition temperature, the strain gradient of SiC films is found to vary from positive to negative when the films change from amorphous to polycrystalline [20]. The strain gradient of polycrystalline films is also reported to be reduced by decreasing the deposition pressure [21]. However, the electrical resistivity is also sensitive to deposition conditions. This makes it challenging to control the strain gradient without compromising the electrical resistivity of the film. For example, for a given NH$_3$/DSB ratio of 0.03, increasing the DSB flow rate from 5 sccm to 7.5 sccm causes the strain gradient to improve from $-4 \times 10^{-4} \mu$m$^{-1}$ to $-3 \times 10^{-5} \mu$m$^{-1}$. However, this film has a higher electrical resistivity of 0.28 Ω cm compared to 0.03 Ω cm obtained on the films deposited at the lower DSB flow rate.

The strain gradient control approach we have developed is by depositing two layers of poly-SiC with different strains obtained by changing the doping content [19]. Specifically, a layer with higher doping content (higher tensile strain) is deposited on the top of a less doped layer (lower tensile strain) to compensate for the negative strain gradient. To preserve the low resistivity, 3% and 5% doped layers are chosen to form the bi-layer films. A 3 μm thick bi-layer film (0.43 μm 5% doped top layer and 2.57 μm 3% doped bottom layer) with a low strain gradient of $5 \times 10^{-3} \mu$m$^{-1}$ has been achieved, while the resistivity of this film is kept at the low value of 0.024 Ω cm.

The strain gradient control by the bi-layer scheme is achieved by a mechanical method, therefore does not inhibit the optimization of other film properties through deposition conditions. In addition, the strain of each layer in this study is controlled by doping content, which has several advantages to the use of deposition temperature to control strain in multi-layer films [23]. First, gas flow can be more quickly adjusted and stabilized than temperature. Second, the constant deposition temperature decreases the possible properties variation of the preceding layer(s) during the deposition of the subsequent layers in the case that the later deposition is carried at higher temperature. The SiC bi-layer films are continuous without large variations in film properties (e.g., microstructure) for various layers; as a consequence, the low strain gradient achieved through this scheme is expected to have good time and temperature stability.

5. Metal contact to poly-SiC

For MEMS applications, the quality of metal contact to poly-SiC film is as important as the electrical and mechanical properties. An ohmic contact of low resistivity with long-term stability in harsh environments is necessary for many practical application of SiC MEMS technology. Nickel and platinum contacts to n-type doped poly-SiC have been characterized by the circular transmission line method (CTLM) at room temperature and up to 300 °C [24]. The as-deposited metal contacts (Ni and Pt) to 3% nitrogen doped polycrystalline SiC films showed ohmic characteristics. The Ni contacts to poly-SiC have the lowest contact resistivity of $1.6 \times 10^{-6}$ Ω cm$^{-2}$, followed by the Pt/SiC contact resistivity of $1.2 \times 10^{-5}$ Ω cm$^{-2}$. Ohmic characteristics have been reported for as-deposited Ni and Pt contacts to n-type single crystalline 3C-SiC films deposited by chemical vapor deposition, although the ohmic contacts are mostly formed after high temperature annealing [25–27]. Although the mechanism of ohmic contact formation has been attributed to the formation of silicides, it has also been proposed that the ohmic contact in Ni/SiC after annealing might be caused by various defects and reduced barrier heights at the interface [28]. We attribute the ohmic characteristic of as-deposited Ni and Pt to nitrogen doped poly-SiC contacts to the polycrystalline nature of the SiC films, which, for example, would possess such defects as grain boundaries and high interface roughness.

The as-deposited Ni/SiC contact resistivity varies with the doping content of poly-SiC films and reaches a minimum value of $1.6 \times 10^{-6}$ Ω cm$^{-2}$ for 3% nitrogen doped film. This film appears the most optimum for MEMS application, due to its lowest contact resistivity and film resistivity. Therefore, the effect of annealing in air at 300 °C on the contact resistivity of this film has been investigated. The contact resistivity measurements are performed at room temperature after 30 min annealing at 300 °C. The Ni/poly-SiC contact resistivity increases dramatically to about $1.3 \times 10^{-5}$ Ω cm$^{-2}$. The Pt/poly-SiC contact resistivity is also found to increase, but only by a factor of 2, to about $2.4 \times 10^{-5}$ Ω cm$^{-2}$. XRD spectra obtained on the Ni/poly-SiC and Pt/poly-SiC after annealing do not show the formation of any nickel silicide or platinum silicide. Furthermore, annealing the Ni/poly-SiC contact at 300 °C for 30 min in a vacuum of $10^{-6}$ Torr does not cause any change in the contact resistivity, suggesting that the observed increase in contact resistivity of Ni/poly-SiC upon annealing in air may be due to the oxidation of the nickel layer, which is supported by the surface chemical analysis by X-ray photoelectron spectroscopy (XPS). To combine low contact resistivity of Ni/SiC and the thermal stability of Pt, a Pt overlayer is applied on the top of Ni/poly-SiC. This contact resistivity, measured at 300 °C in air, only shows an initial increase and eventually stabilizes around $1.2 \times 10^{-5}$ Ω cm$^{-2}$.

6. Conclusion

Nitrogen doped (n-type) and aluminum doped (p-type) polycrystalline SiC are deposited by low pressure chemical
vapor deposition using 1,3-disilabutane single SiC precursor. Resistivity as low as 0.03 Ω cm is achieved by nitrogen doping. Dopant incorporation, carrier transport and temperature effect on resistivity are studied. Negative temperature coefficient of resistivity (TCR) is observed for n-type doped films. The nitrogen doped films possess tensile residual strain and negative strain gradient. A bi-layer deposition scheme consisting of films with different residual strains due to differing doping content is developed to achieve strain gradient as low as 5 × 10^−5 μm−1 without compromising the electrical resistivity of film. Ohmic nickel and platinum contacts to n-type doped poly-SiC are formed at room temperature. A stable metal contact at 300 °C in air is obtained by Pt covered Ni contact to poly-SiC.

References