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Applications of SiC-Based Thin Films in Electronic and MEMS Devices

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1. Introduction

The great development of thin film growth techniques has stimulated the industrial and academic researches about design, fabrication and test of thin film based devices. The replacement of the conventional bulk materials by thin films allows the fabrication of devices with smaller volume and weight, higher flexibility besides lower cost and good performance. It has been shown that the efficiency of thin film based devices is strongly dependent on their structural, electrical, mechanical and optical properties (Fraga, 2011a; Fraga 2012). At the same time that there is a trend in the miniaturization of electronic and electromechanical devices, there is also a considerable interest in the study of wide bandgap materials to replace the silicon as base material in these devices for harsh applications such as high temperatures and high levels of radiation (Fraga, 2012, Yeung, 2007).

Silicon carbide (SiC) has intrinsic properties that make it a material of great interest for microelectronic and MEMS (Micro-Electro-Mechanical Systems) applications. In the last years, there has been much debate in the literature about how the incorporation of dopant elements (such as nitrogen, oxygen, aluminum, boron, phosphorus, etc.) during the growth of SiC thin films by chemical vapor deposition (CVD) or physical vapor deposition (PVD) processes affects their properties. It has been noticed that the dopant incorporation allows controlling thin film properties such as optical bandgap and electrical conductivity, which are quite attractive because make possible to obtain semiconductor or insulator SiC-based films (Alizadeh, 2002; Medeiros, 2011).

In general, the use of amorphous SiC films has been preferred due to relatively their low growth temperature, which guarantees a larger compatibility with silicon-based technology (Hatalis, 1987).

Nowadays, SiC-based thin films, such as SiCN, SiCO, SiCNO, SiCB, SiCBN and SiCP, have been extensively used in electronic and MEMS devices either as a semiconductor or as an insulator, depending on the film composition. These films have been shown promising for applications in diodes, thin-film transistors (TFTs) and MEMS devices (Yih, 1994; Patil, 2003; Hwang, 1995; Fraga, 2011c).

The goal of this chapter is to discuss the role of in situ incorporation of nitrogen, oxygen, aluminum, boron, phosphorus and argon on the properties of SiC films. Special attention is given to the low temperature SiC growth processes. An overview on the applications of SiC-based thin films in electronic and MEMS devices is presented and discussed. Our recent researches on heterojunction diodes and MEMS sensors are emphasized.

2. Dopant incorporation during growth of SiC thin films

2.1. In situ doping

Most studies on SiC thin films, especially in their amorphous form, is not focused on intrinsic films. In general, the electrical properties of wide band gap semiconductor materials as the SiC are controlled by introducing dopants into the bulk material (Oliveira, 2002). Hence, determining the best material doping concentration is one important issue to be considered during a device development. SiC-based thin films with variable electrical conductivity, from semiconductor to insulator, have been produced by adjusting only the dopant concentration. This allows the use of these films in a variety of devices such as solar cells, different diode types, TFTs, MEMS sensors, among others (Vetter, 2006; Oliveira, 2004).

The main chemical elements used as SiC dopants are in group III (aluminum, Al, and boron, B) and group V (nitrogen, N, and phosphorus, P) of the periodic table. Therefore, n-type doping of SiC is commonly achieved by the use of nitrogen or phosphorus whereas p-type is by aluminium or boron. The in situ doping process is done by adding doping gas, such as nitrogen (N_2) or ammonia (NH_3) as nitrogen precursors, diborane (B_2H_6) as boron precursor, phosphine (PH_3) as phosphorus precursor and trimethylaluminum (TMA) as aluminium precursor, during SiC epitaxial growth (Miyajima, 2006). This process is a non-selective doping of SiC epitaxial layers grown on different substrate types (e.g. silicon, silicon-on-insulator (SOI) and quartz) and it has allowed the preparation of SiC films with high electrical conductivity and low defect density. In situ doping exhibits advantages when compared to post-deposition doping methods as ion implantation and thermal diffusion, such as the easy incorporation of dopants in CVD or PVD processes and the reduction of processing steps. It is noteworthy that the incorporation of dopants besides affecting the conductivity of the material also influences other properties namely Young's modulus, hardness, optical gap, transmittance, morphology, etc. (Murooka, 1996; Sundaram, 2004).

In situ doping of amorphous and crystalline SiC films is well-documented in the literature. Historically, the first papers on the electrical properties of a-SiC films were published during the 70's. In 1977, Anderson and Spear investigated the electrical properties of plasma enhanced chemical vapor deposition (PECVD) hydrogenated amorphous SiC (a-SiC:H) films. In the 80's, several papers on doping of a-SiC and a-SiC:H films and their potential applications were published (Tawada, 1982; Beyer 1985; Pereira 1985). Since then, numerous studies have demonstrated the great potential of the SiC-based thin films for electronic device applications.

2.1.1. Nitrogen incorporation

Among the different SiC-based films, the silicon carbonitride (SiCN) has been the most investigated due to its easy synthesis. Generally, SiCN films are produced by introducing nitrogen gas (N_2) during SiC film growth by CVD and PVD processes. The use of N_2 as doping gas is advantageous due to non-toxicity, low cost and high efficiency (Fraga, 2008). The control of N_2 gas flow during deposition process has been shown as a convenient and effective way to change the electrical properties of SiC films in order to obtain films with desired electrical conductivities for each application type. According to Alizadeh and Sundaram, for N_2/Ar ratios from 0.2 to 0.4, the N_2 gas acts like a dopant in a-SiC films prepared onto glass substrate by radiofrequency (RF) magnetron sputtering of a SiC target in N_2/Ar atmosphere, reducing their electrical resistivities from the range of $10^9 \Omega.cm$ to $10^4 \Omega.cm$. However, for N_2/Ar ratios between 0.6 and 0.8 the film resistivity reach values in the range of $10^{10} \Omega.cm$, indicating the formation of insulator SiCN films. Other important correlations between N_2/Ar ratio and the properties of a-SiCN films were shown in their previous work: the bandgap and the percentage of optical transmission of these films increase with the N_2/Ar ratio increases. The electrical conductivity of sputtered a-SiCN films was also studied by Wu et al. where, in this work, the a-SiCN films were deposited onto quartz, glass and Si substrates at room temperature by RF reactive sputtering of a SiC target in $Ar/N_2/H_2/CH_4$ atmosphere. They observed that the dark conductivity decreases with increases in N_2 flow rate. Besides sputtering, other processes are being used to grown a-SiCN films. Gomez et al. used the electron cyclotron resonance (ECR) PECVD to prepare a-SiCN films using nitrogen, methane, and argon diluted silane as precursor gases. Yamamoto et al. investigated the correlation between nitrogen ion energy and the formed chemical bonds in a-SiCN films deposited on (100) Si substrates by nitrogen ion-assisted pulsed-laser ablation of a SiC target.

In situ nitrogen doping of crystalline SiC films have also been commonly reported. Wijesundara et al. investigated the nitrogen doping of polycrystalline 3C-SiC films grown on (100) Si substrates by LPCVD at various growth temperatures 650–850°C using 1,3-disilabutane and NH_3 as precursors. They concluded that the electrical resistivity of the polycrystalline films is further controlled by adjusting the NH_3 flow rate in the reactor and that nitrogen-doped 3C-SiC films exhibit lower resistivities (around $0.02 \Omega.cm$) than the undoped (around $10 \Omega.cm$) obtained at 800°C. The effects of N_2 flow rate and growth temperature on the electrical properties of nitrogen-doped 3C-SiC thin films, grown on $Si_3N_4/p-Si$ (111) substrates by LPCVD at temperature 1100-1250°C using organosilane-precursor trimethylsilane ($(CH_3)_3SiH$), were discussed by Cheng et al. It was observed that independent of the temper-

ature process the film resistivity decreases continuously with N_2 flow increases. Liu et al. reported the synthesis of nitrogen-doped polycrystalline 3C-SiC thin films by LPCVD at 800°C with optimized properties for MEMS applications: resistivity of 0.026 $\Omega\cdot\text{cm}$, residual stress of 254 MPa and strain of 4.5×10^{-4} . The deposition conditions to produce films with these characteristics were established through studies on the effects of the precursor gases flow rate, NH_3 and diclorosilane, on the material properties such resistivity, residual stress, strain, crystallinity and surface morphology. It is necessary to underline that for crystalline SiC films prepared by CVD processes, the site-competition epitaxy model has been shown as an efficient method to control in situ doping. This model is based on the variation of the Si/C ratio within the CVD reactor in order to control the dopant incorporation. In the case of the nitrogen doping in SiC, its incorporation is directly related to Si/C ratio (Larkin, 1997).

2.1.2. Phosphorus incorporation

In situ phosphorus doping, although little used, is another way used to obtain n-type SiC. Ruddell et al. employed a thermal CVD reactor for the deposition of phosphorus-doped SiC layers on Si substrates using silane/propane/phosphine gas chemistry over the temperature range 720-970°C. SiC films with a phosphorus concentration of $5 \times 10^{20} \text{ cm}^{-3}$ and resistivity of 0.6 $\Omega\cdot\text{cm}$ were obtained, which indicates a good efficiency of phosphorus doping. The correlations between the microwave power (from 150 to 900 W) and the properties of phosphorus-doped SiC:H films, prepared by ECR-CVD from a mixture of methane/silane/ hydrogen/ phosphine, were investigated by Yoon et al. The properties of n-type nanocrystalline hydrogenated cubic silicon carbide (nc-3C-SiC:H) prepared by hot-wire chemical vapor deposition (HWCVD), using phosphine and hexamethyldisilazane (HMDS) as dopants, at low temperatures around 300°C were studied by Miyajima et al. In situ phosphorus doping during sputtering process was reported by Pereira et al. that performed the substitutional doping of RF sputtered amorphous SiC by adding controlled amounts of phosphine (PH_3) to the argon atmosphere at a constant substrate temperature of 200 °C. They observed that the conductivity of the SiC film increases about one order of magnitude when doped with phosphorus and in the presence of 0.5 m Torr of hydrogen. In recent work, Loubet et al. reported an epitaxy process based on a cyclical deposition-etch (CDE) technique to obtain ultra-low resistivity in situ phosphorus-doped silicon carbon (SiCP) layers for raised source/drain applications. Despite studies have demonstrating the efficiency of in situ phosphorus doping during SiC film growth, this process is not much used due to high toxicity and flammability of PH_3 gas. When used, in general, PH_3 is highly diluted (< 1%) in hydrogen because the risks in diluted form are less critical.

2.1.3. Aluminum incorporation

Considerable efforts have also been made to prepare p-type SiC films. In situ aluminum doping of SiC films is one of the processes used for this purpose. Wang et al. presented a doping method for growth of Al-doped single-crystalline 3C-SiC epilayers onto (100) Si substrates by atomic-layer epitaxy at 1000°C using silane, acetylene and TMA gases in a conventional LPCVD reactor. The hot-probe and Hall effect measurements confirmed that the

Al-doped SiC are of p-type conductivity. The film resistivity, measured at room temperature by a standard four-point probe system, was of 0.31 $\Omega\cdot\text{cm}$. Sha et al. discussed the photoluminescence properties of Al-doped SiC films deposited on Si substrates by RF magnetron sputtering of a single crystalline SiC target containing several pieces of aluminum on its surface. The influence of substrate temperature (300–390°C) on the aluminum doping of $\mu\text{c-SiC:H}$ prepared by hot-wire CVD using TMA as gas dopant was discussed by Chen et al.. They concluded that a process temperature higher than 350°C is needed to obtain effective aluminum doping of $\mu\text{c-SiC:H}$ thin films. An important observation on in situ aluminum doping in SiC is that according to the site-competition epitaxy model, the Al dopant incorporation has been found to be inversely related to the Si/C ratio within the CVD reactor. This behavior is opposite to that observed in nitrogen incorporation in SiC (Larkin, 1997).

2.1.4. Boron incorporation

In situ boron doping is other process used to obtain SiC films with p-type conductivity. Boron-doped sputtered a-SiC:H films, prepared onto corning glass and c-Si substrates maintained at temperatures of 125–250°C by magnetron sputtering of silicon in $\text{Ar}+\text{H}_2+\text{B}(\text{CH}_3)_3$ atmospheres, were reported by Uthanna et al. The highest values of dark conductivity and doping efficiency were achieved at a carbon content $x=0.04$. It was also found that the film with $x=0.14$, deposited at 175°C, has electrical properties as required for solar cell applications. Yoon et al. studied the effects of the diborane (B_2H_6) levels on the deposition rate, optical band gap and conductivity of boron-doped SiC:H films prepared using ECR PECVD technique from a mixture of methane, silane, hydrogen and diborane gases. It was observed that at a low microwave power of 150 W the band gap of the SiC:H film decreases as the diborane flow increases, whereas the films deposited at a high microwave power of 800 W remains relatively unaffected throughout the entire range of diborane levels investigated. Highly conductive boron-doped nanocrystalline SiC films with a low concentration of hydrogen-dilution (p-nc-SiC:H) grown by a mercury-sensitized photo-CVD method using silane, hydrogen, diborane and ethylene as a carbon source, were reported by Myong et al. These films were tested as window material for amorphous silicon solar cells and a good conversion efficiency of 10.4%, without use any back reflectors, was obtained. It has also been noticed the improvement of the Young's modulus of polycrystalline SiC film grown by LPCVD through the introduction of B_2H_6 in the precursor gas mixture (Murooka, 1996). This study concluded that the Young's modulus of SiC films increases with the addition of B_2H_6 , and a maximum value of 600 GPa, which was 25% higher than in the case without B_2H_6 , was reached at a source gas ratio $\text{B/Si}=0.02$.

Although boron-doped SiC films exhibit suitable properties for different applications, these films are still little used because, like the PH_3 , the B_2H_6 dopant gas is toxic. An alternative method for the formation of SiCB films has been shown in the literature: the deposition of SiCB films using sputtering target containing boron in its composition. This method has also allowed the growth of quaternary compound SiCBN by introducing N_2 gas into deposition process. Optical properties of amorphous SiCBN thin films obtained, by co-sputtering from SiC and BN targets using N_2/Ar gas mixtures, were studied by Vijayakumar et al. It was

found that the transmittance of the SiCBN films increases with nitrogen incorporation increases. Petrman et al. prepared SiBCN films by reactive magnetron sputtering of a $\text{Si}_{-75}(\text{B}_4\text{C})_{25}$ target in N_2/Ar gas mixtures. They showed the dependence of electrical resistivity and optical gap of SiBCN films on the N_2 content used in the N_2/Ar gas mixture.

2.2. Unintentional doping

The incorporation of dopants during SiC growth can also be unintentional, i.e., when elements presented during the deposition process are incorporated into film due to unwanted chemical reactions. Oxygen and hydrogen have been shown as the most common unintentional dopants of SiC films.

The contamination sources by hydrogen are well clear. It is known that the presence of hydrogen in the plasma and its consequent incorporation into the SiC film, in CVD or PVD deposition processes, is due to use of hydrogenated precursor gases as source of carbon (e.g. CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10}) and as source of silicon (e.g. SiH_4 and Si_2H_6). The hydrogen incorporation is significant, when the SiC films are produced at low temperature processes as PECVD and sputtering. This has motivated several studies on how the hydrogen incorporation affects the properties of SiC films and on the applications of a-SiC:H films in devices. Studies on PECVD and sputtered a-SiC:H films have shown that the hydrogen incorporation induces the formation of voids (Beyer, 1985) and increases the compressive stress (Kim, 1995). On the other hand, increasing hydrogen content in a-SiC:H films increases the optical gap (Shimada, 1979), improves the photoconductivity and increases the electrical resistivity. The optical and electrical changes due to hydrogen incorporation have stimulated the research on growth of a-SiC:H films by using the hydrogen dilution method, i.e, adding hydrogen gas (H_2) to the deposition process. This method is attractive because the optical gap of the a-SiC:H films can be varied by changing the H_2 flow rate while the other deposition parameters are kept constant. In recent years, a-SiC:H films have been successfully employed as electronic surface passivation of c-Si in photovoltaic applications exhibiting performance comparable to thermal SiO_2 and a-SiN_x that are the most used materials. As the photoconductivity of a-SiC:H films is high, another attractive application of these films is replacing Si:H top layer of pin solar cells (Vetter, 2006).

Regarding the unintentional contamination by oxygen, the sources have been more discussed in the literature. Many studies have showed that the oxygen contamination sources during the deposition of SiC films are mainly the residual gas in reactant chambers, possible air leak in the deposition system and adsorbed gas molecules on the reactor inner walls (Medeiros, 2011). Moreover, post-deposition film surface contamination by oxygen, that can occurs when the SiC film is exposed to atmospheric air, has also been described by different authors (Fraga, 2008). The oxygen incorporation in SiC films and the consequent formation of silicon oxycarbide (SiCO) can be interesting for different applications such as thin film anodes for lithium ion batteries (Shen, 2011) and as doping contacts for solar cell applications (Martins, 1996). The excellent physical and chemical properties identified in SiCO films have motivated studies on the growth and characterization of these films intentionally deposited through oxygen gas addition during their growth process. Amorphous SiCO films have been produced mainly by sputtering of a SiC target in O_2/Ar atmosphere or by PECVD using

$C_xH_y/Si_xH_y/O_2$ gas mixture which result at hydrogenated films (a-SiCO:H). It has been reported that these films exhibit mechanical and electrical properties strongly dependent of the oxygen-to-carbon ratio in their chemical composition. A potential application of SiCO and SiCO:H films is to replace SiO_2 in microelectronic devices because it possesses advantages over other lower dielectric materials since it is formed as an interface phase between SiC and SiO_2 . Apart from applications in surface passivation, dielectric insulation and copper diffusion barrier, SiCO films have also been used in photodetectors and for oxygen detection in high temperature and corrosive environments. The literature also shows the synthesis of silicon oxycarbonitride (SiCNO) films by unintentional oxygen incorporation during low temperature reactive magnetron co-sputtering of silicon and graphite targets in mixed Ar/N_2 atmosphere (Medeiros, 2011). As others SiC-based films, SiCNO films exhibit high thermal stability, tunable bandgap characteristics and high gauge factor values (Cross, 2010; Ter-auds, 2010). A comparison among the physical, electrical, and reliability characteristics of SiC, SiCN, SiCO, SiCNO and SiN thin films was performed by Chen et al. It was observed that SiCNO films are the most appropriate to be used as copper diffusion barrier because exhibit more reliable electro-migration and stress-migration besides to present physical and electrical performance comparable to those of SiN films.

Although less studied, the argon is another atom that can be incorporated during the growth of SiC films. For this, bias assisted CVD or PVD technique with high potentials applied to the substrate holder allows tuning the argon ion (Ar^+) flux on the substrate surface and, consequently, the concentration of incorporated argon into film. Some studies on chemical composition of SiC films using RBS and XPS analysis have indicated argon content up to 8 at.% in film composition. A.K. Costa and co-workers investigated the influence of the substrate negative bias increases (from 0 to -100 V) on the properties of sputtered SiC films. They observed that the substrate bias leads to substantial argon incorporation into the SiC film, which results in the increase of the hardness. A negative characteristic was also observed. The microscopic examination of the film surface showed a large number of defects and pinholes as the argon content increases together with a reduction in the deposition rate due to the sputtering of the film surface by argon ions. In a recent work, Medeiros et al. showed that increasing the argon incorporated in Si_xC_y films, deposited onto (100) Si by dc magnetron co-sputtering technique under different negative substrate bias, promotes an increase of the elastic modulus and a reduction of the electrical resistivity. In addition, it is also noticed that co-sputtered Si_xC_y films grown at high negative substrate bias (between -100 and -300 V) are free of oxygen contamination.

3. Challenges and trends of the growth processes of SiC thin films

The main motivation to use thin films is simple: easy growth on a wide variety of substrates. In the case of the SiC, the use of thin films includes other motivations: (a) the cost of SiC bulk substrates is still high; (b) the defect density is relatively high and (c) the area of the substrate available is still small (Fraga, 2011d).

Nowadays, the SiC devices are categorized into two groups: one uses SiC bulks and the other uses SiC thin films grown on Si or insulator/Si substrates. In general, comparative studies

show that devices based on SiC bulk substrates exhibit better performance than those thin film based (Harris, 1995). Then, the first challenge is to grown SiC thin films with properties as good as the bulk substrate. In addition, it is necessary to achieve high film growth rate as well as thickness uniformity and homogeneity when deposited on large-area Si wafers, which are important factors to reduce costs. For this, the influence of SiC growth process parameters, such as gases flow rate, substrate temperature, pressure and doping, have been evaluated and optimized.

The literature has shown that devices based on thin films, grown on the same conditions, often did not exhibit similar performance (Fraga, 2012). Identify and overcome the causes of the non-reproducibility is another challenge. The synthesis of high-quality SiC films with reproducible properties is fundamental for the advancement of the SiC thin film device technology. It is known that the properties of thin films are strongly dependent on the deposition conditions, i.e., the repeatable and precise control of deposition conditions is important to ensure the reproducibility film. The electrical resistivity and thickness measurements of films, deposited under same conditions, are the most used parameters to evaluate their reproducibility.

Extensive research has been done on growth of SiC films at low or high temperature process aiming to produce high quality films. Three methods have been most frequently used: CVD, PECVD and sputtering. Table 1 compares these methods. The most critical issue facing CVD SiC films for device applications is the high temperature necessary to assure the surface reactions and good deposition rate (Ong, 2006). The low temperature deposition is very important from the point of view of device integration. The synthesis of low-temperature deposited highly-conductive SiC films has been a goal of many research groups focused on the development of TFTs, solar cells and heterojunction bipolar transistors (Cheng, 1997). This has encouraged more studies on the optimization of low-temperature methods as PECVD and the different sputtering processes. PECVD SiC films have been deposited at a relatively low temperature (less than 300°C). The films present a good adhesion, high deposition rate and good uniformity. Sputtering process presents poor sidewall coverage due to the significant distance between the target and the substrate. Besides, the deposition is frequently made at room temperature and usually has a low deposition rate (Ong, 2006).

	CVD	PECVD	Sputtering
Cost	Fair	Fair	Fair
Uniformity	Fair	Fair	Fair
Substrate versatility	Good	Very good	Very good
Stress control	Poor	Very poor	Good
Throughput	Varies	Very good	Fair

Table 1. Comparison among the main methods used to grown SiC films.

To illustrate the comparison among PECVD and sputtering, we will discuss the results obtained in our works on SiC films grown by PECVD and RF magnetron sputtering. Regarding the throughput of the method, we have found high PECVD SiC film growth rate, from 24 to 36 nm/min, depending on SiH_4/CH_4 flow rate used (Fraga, 2007) and from 4.0 to 7.0 nm/min for films deposited by RF magnetron sputtering of a SiC target under different Ar/N_2 mixtures (Fraga, 2008). In order to evaluate the uniformity, the following tests were performed: (a) before the SiC film deposition, three small steps were created by placing strips on different points of the 2 inch p-type Si wafers, (b) after the deposition, each wafer was cut in fourth path equals, (c) the thicknesses and resistivities of the paths were measured by profilometry and four-points probe, respectively. It was found: thicknesses between 432 and 470 nm and resistivities between 12 and 16 $\Omega\cdot\text{cm}$ for the pieces of PECVD SiC film, whereas for the sputtered films between thicknesses 337 and 385 nm and resistivities between 0.2 and 0.25 $\text{M}\Omega\cdot\text{cm}$. These results indicate that the throughput of PECVD is considerably greater than of RF magnetron sputtering. However, both methods present problems in terms of film uniformity. It is noteworthy that our tests were performed with 2 inch Si wafers whereas the semiconductor industries have been using up to 12 inch wafers. It is likely that the problems of uniformity are more significant in substrates with larger dimensions.

The residual stress control of SiC thin films is another issue, which can also be added to the challenges. It has been demonstrated that SiC film stress can affect the sensitivity, precision and functionality of thin-film based devices, thus, in some applications, is important to have a low residual stress.

SiC film deposition process	Young's modulus (GPa)	Reference
APCVD	450	Zorman, 1995
LPCVD	396	Fu, 2004
PECVD	88 to 153	El Khakani, 1994
PECVD	56	Flannery, 1998
PECVD	196	Cros, 1997
RF triode sputtering	231	El Khakani, 1994
RF magnetron sputtering	363	Singh, 2012
Co-sputtering	245 to 377	Medeiros, 2012

Table 2. Young's modulus reported in the literature for SiC films grown on Si substrates.

Initially, the research efforts on semiconductor and dielectric thin films were focused on their electrical properties in order to satisfy the demand in microelectronic devices industry. In general, studies on mechanical properties were limited to internal stress measurements (Tsuchiya, 2008). With the advent of microelectromechanical system (MEMS) technology, the thin films started to be used as mechanical structures, which made fundamental the knowledge of their mechanical and electromechanical properties. The high Young's (or elas-

tic) modulus is the key mechanical property to use them as structural layer in MEMS devices. As can be observed in Table 2, crystalline and polycrystalline SiC films grown by atmospheric pressure chemical vapor deposition (APCVD) and LPCVD processes exhibit higher Young's modulus than the amorphous produced at low temperatures by PECVD and sputtering. In addition, it has been observed that the most of the SiC films still exhibit lower Young's modulus than the reported for SiC wafers which is in the range between 330 and 700 GPa depending on the polytype (Zorman and Parro, 2010).

One issue that should be considered is that, although the researches on SiC film growth have been mainly focused on the deposition of SiC on Si substrates, MEMS applications frequently require the growth of SiC thin films on sacrificial and insulating layers, as for example SiO_2 or Si_3N_4 , grown on Si substrates. Thus, to evaluate the influence of substrate type on the properties of SiC films is another important point. Some works have investigated the growth and properties of SiC films on SiO_2 , Si_3N_4 and poly-Si (Fleischman, 1998; Wu, 1999; Chen, 2000). A known drawback of SiC on insulator layers is the high stress caused by the large lattice and thermal mismatch between SiC and insulator, which become post-deposition annealing necessary to minimize this problem and improve the quality SiC film on insulator. Other particularities of SiC growth on insulator/Si substrates include: the effect of insulator layer thickness on the properties of SiC film and the choice of the suitable insulator for each device application. Chen et al. reported the SiC growth by CVD on the following substrates: thermally oxidized Si substrates with SiO_2 thicknesses of 30, 50, 70, and 100 nm, Si substrates with native oxide of 2 nm and 3 μm thick phosphosilicate glass (PSG). They observed that in the thickness range between 30 and 70 nm, the SiO_2 serves as a compliant layer which reduces the strain between SiC film and the substrate besides allows the growth of a more oriented SiC film. In relation to choice of the insulator, Si_3N_4 has shown more suitable than SiO_2 due to: (i) its higher dielectric constant that can reduce the leakage currents, and (ii) its thermal expansion coefficient is much closer to that of SiC than one of SiO_2 , thus the stress in SiC film grown on Si_3N_4 will be lower than that on SiO_2 (Cheng, 2003). Nevertheless, most of the SiC thin-film MEMS devices reported in the literature use the SiO_2 as sacrificial layer and/or substrate electrical isolation (Chang, 2008; Mishra, 2009). One reason for this is the easy formation of SiO_2 achieved by thermal oxidation of Si substrates.

In our researches, we have explored the properties of SiC thin films grown on SiO_2/Si substrates by PECVD and RF magnetron sputtering for the development of strain gauges (Fraga, 2010) and pressure sensors (Fraga, 2011a; Fraga 2011c). Young's modulus was found to be 65 GPa for PECVD a-SiC film and 57 GPa for nitrogen-doped PECVD a-SiC film. These values are near to 56 GPa that was reported for PECVD a-SiC film grown on Si substrates (Flannery, 1998). On the other hand, the Young's modulus values found by us for RF-sputtered SiC and SiCN films on SiO_2/Si were considerably lower than those reported in the literature for films on Si substrates. We found Young's modulus of 40 GPa and 88 GPa for sputtered a-SiC and SiCN films respectively, whereas other authors have found values above 200 GPa for sputtered SiC film grown on Si (see Table 2) and 117 GPa for SiCN film grown on Si (Sundaram, 2004). For CVD processes, the following Young's modulus was

found: 426 ± 100 GPa for SiC grown on SiO₂/Si by APCVD (Fleischman, 1998) and 426 GPa for SiC grown on Si₃N₄/Si by LPCVD (Cheng, 2002).

In general, the literature has shown that the substrate type influences the structure, morphology, electrical and mechanical properties of SiC films. However, although there are differences related to the substrate type, the properties, such as high Young's modulus, high chemical resistance and high thermal stability among others, that make the SiC film attractive for a variety of harsh environment MEMS device applications are maintained.

4. SiC thin film based electronic devices: diodes and TFTs

4.1. Diodes

4.1.1. Heterojunction diodes

A SiC/Si heterojunction diode is formed by the growth of a SiC thin film with opposite doping impurities to the Si substrate used. Thus, it forms a p-n heterojunction with principle similar to a homojunction. However, the energy band for a heterojunction diode is much more complicated than that of a p-n homojunction because uses two semiconductors of different band gaps (Li, 2006).

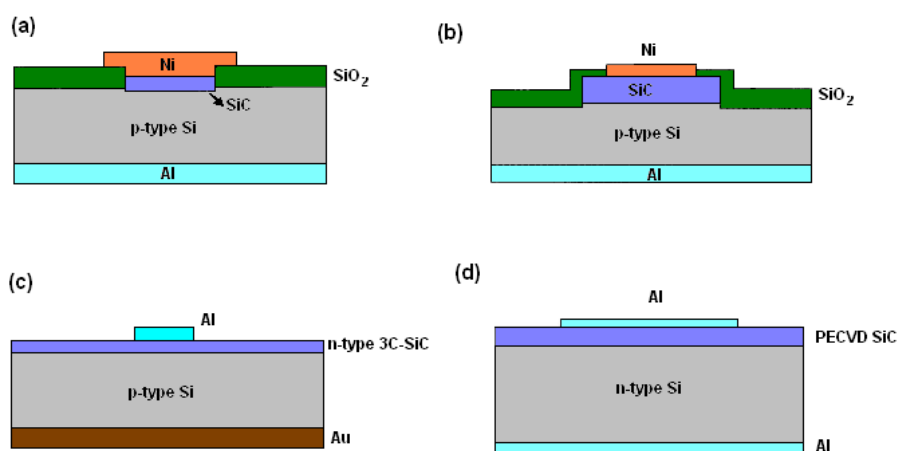


Figure 1. Schematic illustration of cross-section of heterojunction diode structures reported in literature: (a) and (b) Yih et al., (c) Chung and Ahn, (d) Oliveira et al.

The SiC/Si heterojunction diodes with high breakdown voltage and performance dependent on the quality of the SiC film used have been reported in the literature. Yih et al. developed SiC/Si heterojunction diodes using two different rapid thermal chemical vapor deposition (RTCVD) processes: one through the formation of crystalline β -SiC by propane carbonization of the Si substrate in regions unprotected by SiO₂ layer forming planar diodes, as shown in Figure 1 (a), and another by growing polycrystalline β -SiC through the decomposition of

methyilsilane (CH_3SiH_3) at 1300°C forming mesa diodes, Figure 1 (b). Both diodes used Ni on the SiC film as ohmic contact and Al on Si as backside contact. These SiC/Si heterojunction diodes, for both device configurations, exhibit good rectifying properties. Reverse breakdown voltages of 50 V and 150 V were obtained for the planar and mesa heterojunction diodes, respectively. These results demonstrated the potential use of SiC/Si heterojunction for the fabrication of bipolar transistor.

A 3C-SiC/Si heterojunction diode fabricated by a more simple process was reported by Chung and Ahn. This diode was fabricated by the deposition of poly 3C-SiC thin films on p-type substrates using Ar, H_2 and HMDS gases in an APCVD system at 1100°C . The ohmic contacts were prepared by the deposition of Al circle electrodes on poly 3C-SiC surface and an Au layer on the Si substrate side. Figure 1 (c) shows schematic diagram of the 3C-SiC/Si heterojunction diode formed. They concluded that p-n junction diode fabricated by poly 3C-SiC film has similar characteristics to single 3C-SiC p-n junction diode.

Although studies have shown that the deposition of SiC films on Si substrates at low temperatures processes results in heterojunctions with low breakdown voltage and high reverse leakage current, Oliveira et al. developed PECVD SiC/Si heterojunction diodes (Figure 1 (d)) with satisfactory electrical performance exhibiting good rectifying properties. An interesting conclusion of this work is that the post-deposition thermal annealing improves the electrical properties of the PECVD SiC films. It was observed that the heterojunction formed by annealed PECVD SiC film, at 550°C for 120 min, has a leakage current approximately one order of magnitude smaller than that formed by as-deposited films.

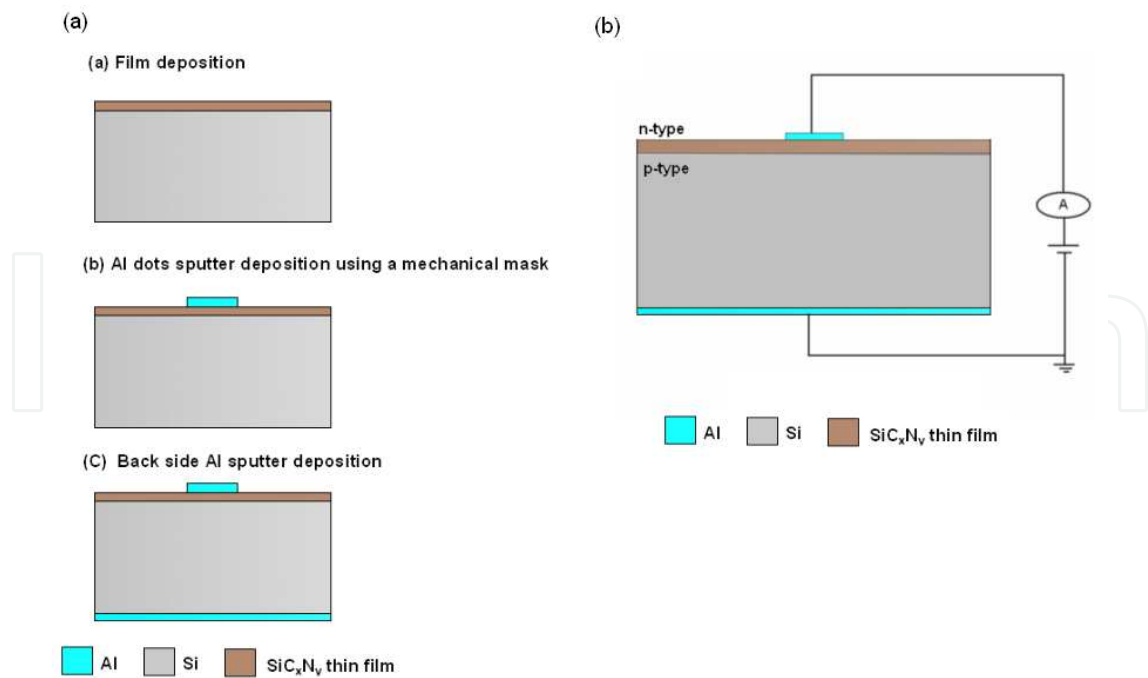


Figure 2. $\text{SiC}_x\text{N}_y/\text{Si}$ heterojunction diode: (a) Sequence of fabrication and (b) schematic diagram of electrical characterization.

We have also studied heterojunctions formed at low temperatures using RF magnetron sputtering of a SiC target under different N_2/Ar gas flow ratio (from 0.1 to 0.3) to prepare a-SiC_xN_y film with different compositions on p-type (100) Si substrates (Fraga, 2011b). After deposition, the films were submitted to a thermal annealing at 1000°C for 30 min. The n-type conductivity of the sputtered a-SiC_xN_y thin films was verified by hot probe technique. The electrical contacts were fabricated through deposition of Al dots on the a-SiC_xN_y surface and subsequently a layer of Al was sputtered on the back side of Si substrate (see Fig. 2 (a)). The a-SiC_xN_y film thicknesses are between 320 and 350 nm, whereas the Al layers have thicknesses around 225 nm. The motivation of this study was evaluate the influence of film composition on I-V characteristics of a-SiC_xN_y/Si heterojunction diodes. The I-V characteristics were measured using an Agilent B1500A semiconductor.

The analyses were performed in a voltage range from -10 to +10 V at room temperature. As can be observed in Figure 3, the N_2/Ar flow ratio increases from 0.1 to 0.2 reduced the electrical current in three orders of magnitude (from mA to μA). On the other hand, the current was not affected significantly increasing the N_2/Ar flow ratio from 0.2 to 0.3.

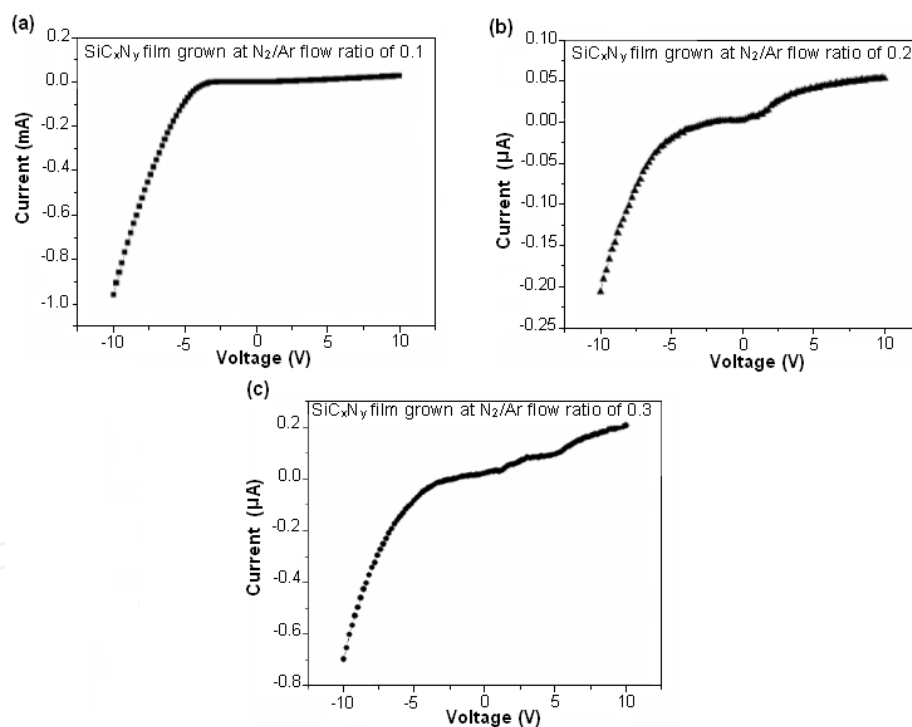


Figure 3. I-V characteristics of a-SiC_xN_y/Si heterojunction diodes at room temperature.

Regarding the temperature effects, the I-V characteristics at different temperatures of the a-SiC_xN_y/Si heterojunction diode, fabricated with the a-SiC_xN_y deposited at N_2/Ar of 0.1, is shown in Figure 4. It was observed that the electrical current increases when the temperature is increased from 35 to 135 °C. However, at temperature of 160 °C there is an almost overlap with the curve obtained at 135°C.

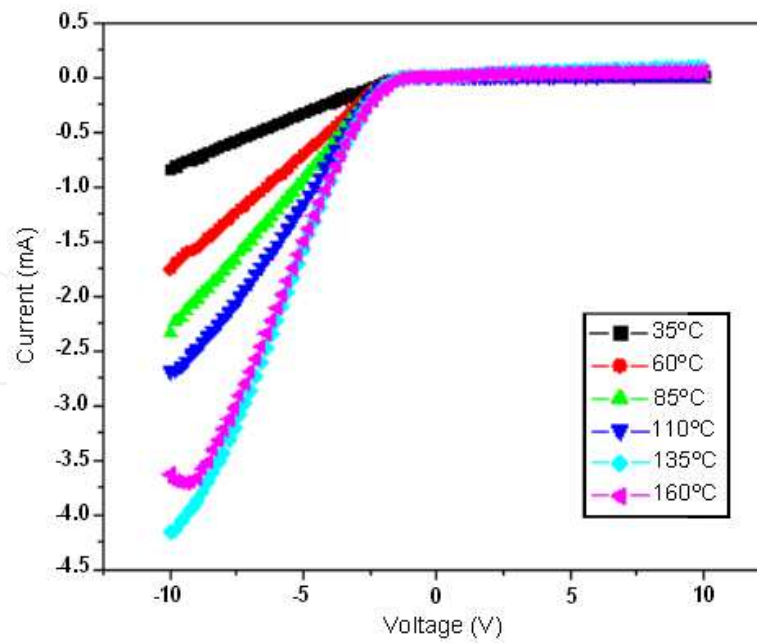


Figure 4. I-V characteristics of a-SiC_xN_y/Si heterojunction diode (N₂/Ar flow ratio= 0.1) at different temperatures.

4.1.2. Other diode types

SiC thin film electronic devices also include Schottky diode and light emitting diode (LED). Komiyama et al. fabricated Schottky diodes through the heteroepitaxial growth of 3C-SiC on a (001) Si substrate by introducing low-temperature growth (700–900°C) of 3C-SiC using methylsilane single source, as an intermediate buffer layer, prior to the subsequent 3C-SiC active layer growth at a higher temperature (1150 °C) using SiH₄ and C₃H₈ as precursors. The diode achieved a breakdown voltage of 190 V. A correlation between the film thickness and the leakage current of the Schottky diode was observed: on reverse bias the leakage current decreases when the 3C-SiC film thickness is increased. Figure 5 (a) shows the Schottky diode with Au,Al/poly 3C-SiC/SiO₂/Si substrate structure developed by Chung and Ahn. This diode exhibited a breakdown voltage of over 140 V together with a high leakage current. The authors suggested that the problem of the high leakage current is associated to random grooves, due to existence of anti-phase boundaries (APB) in the poly 3C-SiC film which demonstrates the dependence between the diode performance and the film characteristics.

Wahab et al. reported a Schottky diode formed by β-SiC thin films grown on (100) Si substrates, using reactive magnetron sputtering of a Si target in CH₄/Ar mixed plasma, with Au electrical contacts. Good electrical properties were observed such as ideality factor of 1.27 and leakage current density of 4 μA/cm².

A hot wire deposited a-SiC:H based thin film light emitting p-i-n diode was fabricated by Patil et al. The diode structure is formed by glass/TCO (SnO:F)/p-a-SiC:H/i-SiC:H/n-a-SiC:H/Al as illustrated in Figure 5 (b). The p-type a-SiC:H film was grown using SiH₄/C₂H₂/B₂H₆ gas mixture, the n-type using SiH₄/C₂H₂/PH₃ and the intrinsic using SiH₄/C₂H₂.

The deposition conditions of each film were optimized to obtain the p-, i- and the n-layers with desired electrical and optical properties. The layers exhibit the following bandgaps: 2.0 eV for p-type a-SiC:H, 2.06 for n-type a-SiC:H and 3.4 eV for intrinsic a-SiC:H.

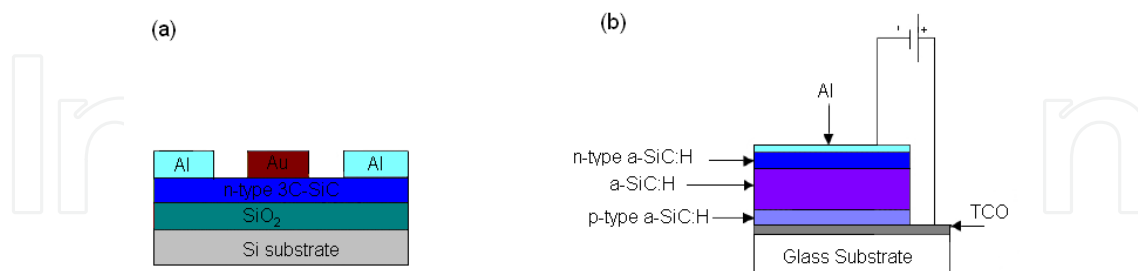


Figure 5. Schematic illustration of cross-section of device structures: (a) Schottky diode and (b) light emitting diode.

The diode was characterized and emits light in the visible region with low intensity. The authors attributed the low emission efficiency to the fact of the device be made in a single chamber and the same filament has been used to deposit all the a-SiC:H layers, which can has caused the contamination across the p-i interface.

4.2. Thin-film transistors (TFTs)

For many years the SiC thin film transistors prepared at low temperature have attracted special attention. In 1994, Hwang et al. developed two models of SiC submicron MOSFETs with vertical channel. The first model, as illustrated in Figure 6 (a), uses a sputtered SiC thin film, grown on a Si substrate at 600°C and annealed at 1300°C for 5 h under Ar atmosphere, as channel layer. It was observed that this structure can attain higher current, but the I-V characteristics can not be saturated because the channel depth is too large to be depleted. The second model fabricated (Figure 6 (b)) is formed by SiC thin film deposited by RF sputtering at 600°C on the sidewall of SiO₂ insulator. With this model, a complete saturation was achieved at drain voltage of 8 V for a 400 nm channel length. Furthermore, a drain breakdown voltage more than 16 V was achieved due to the wide bandgap of the SiC film used (2.2 eV). Both models were characterized under 600 K and the I-V curves do not show turn-off indicating that the TFTs fabricated can operate in this temperature range.

In 2006, Garcia et al. reported the first PECVD amorphous silicon carbide TFTs. The a-Si_{1-x}C_x:H films were deposited on glass substrates by PECVD at 300°C using SiH₄/CH₄/H₂ gas mixture. Subsequently, n-type a-Si:H layer was deposited using SiH₄/H₂/PH₃ gas mixture and a photolithography was performed. Then, a PECVD SiO₂ layer, for the gate dielectric, was deposited using SiH₄/N₂O and a second photolithography was performed. The metal contacts were formed through the deposition of an Al layer followed by photolithography. Finally, an annealing in H₂ atmosphere at 350°C was performed for 30 min. The TFT structure obtained is illustrated in Figure 6 (c). The TFT was tested at different temperatures. The drain current increased two orders of magnitude as temperature increased from 30°C to

200°C. This work compared this $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ TFT with a polycrystalline TFT fabricated by a KrF excimer laser annealing of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films. The polycrystalline TFT exhibited output current at least an order of magnitude higher, when operated at room temperature, with respect to its amorphous being $V_{\text{GS}} = 10 \text{ V}$ for both.

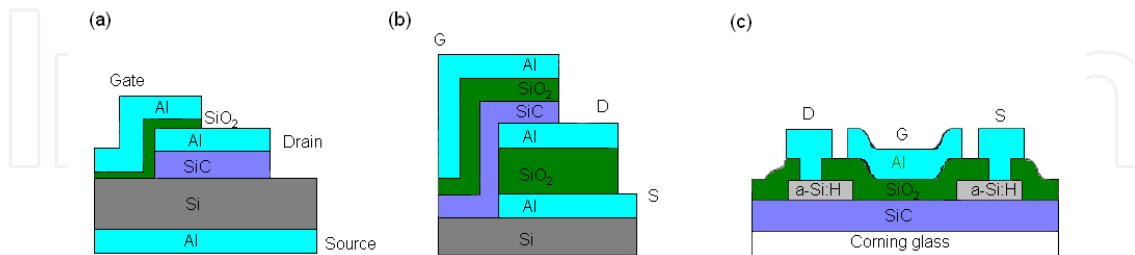


Figure 6. Schematic illustration of cross-section of TFT structures reported in literature: (a) and (b) Hwang et al., (c) Garcia et al.

5. SiC thin film based MEMS devices: sensors, RF MEMS and BioMEMS

5.1. Piezoresistive and capacitive sensors

It is well known that silicon piezoresistive sensors can not be used for high-temperature applications because of the p-n insulation of the piezoresistors. Several studies have demonstrated that the use SiC thin film piezoresistors is a good alternative for these applications due to their high gauge factor together with thermal stability. Ziermann et al. developed a piezoresistive $\beta\text{-SiC}$ -on-silicon on insulator (SOI) pressure sensor with an on chip polycrystalline SiC thermistor for high operating temperatures. The test results from room temperature to 573 K demonstrated the capability of this sensor to monitor the cylinder pressure of combustion engines. We have studied the piezoresistive properties of amorphous SiC ($a\text{-SiC}$) films produced at low temperatures by PECVD and magnetron sputtering (Fraga, 2011d). Figure 7 (a) illustrates a piezoresistive pressure sensor with $a\text{-SiC}$ piezoresistors developed by us.

In 2004, Young et al. proposed single-crystal 3C-SiC capacitive pressure sensors (see schematic illustration shown in Figure 7(b)) for sensing capabilities up to 400°C. The fabrication of polycrystalline 3C-SiC capacitive pressure sensors was reported by Du et al. More recently, Chen and Mehregany reported the first all-SiC capacitive pressure sensor, incorporating a SiC diaphragm on a SiC substrate. Measurements of pressures up to 700 psi and temperatures up to 574°C were demonstrated. This shows that thin film-based technology has a lot to be developed to achieve the performance of sensors based on bulk materials.

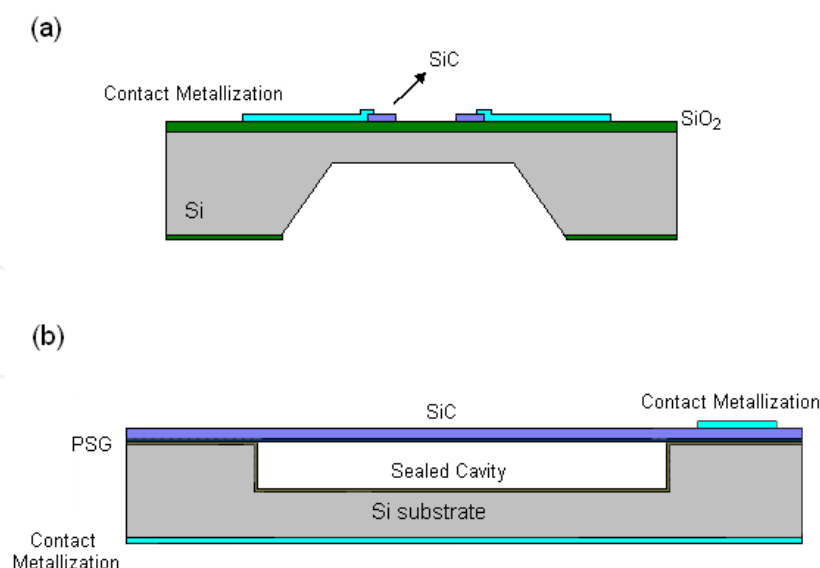


Figure 7. Examples of SiC film sensors shown in the literature: (a) piezoresistive and (b) capacitive.

5.2. RF MEMS

SiC films have been shown as a good alternative to the metal films in radiofrequency micro-electromechanical systems (RF MEMS) applications, especially microbridge-based RF MEMS switches (Parro, 2008; Mishra, 2009) and MEMS resonators (Chang and Zorman, 2008).

Mishra et al. proposed a MEMS switch with low actuation voltage as illustrated in Figure 8 (a). This model uses a beam that is made of two materials: the SiC film to give mechanical stability and the Au to provide the conducting path to the ground. A process using four masks was employed to fabricate it: a high-resistivity p-type (100) Si wafer with 1.0 μm thermal SiO₂ was used as substrate, 800 nm of Au was deposited and patterned using lift-off to define the coplanar waveguide (CPW), to form the switch, a 1.5 μm of polyimide sacrificial layer was spun, soft-baked, and patterned to define the anchors. The anchors and the beam are made by depositing a 0.3 μm and 0.9 μm layers of SiC and Au, subsequent etching of the polyimide sacrificial layer. The switch exhibited an isolation of -40 db at 10 GHz and pull down voltage of 3 V.

The single-crystal and polycrystalline 3C-SiC lateral resonators were developed by Chang and Zorman. An illustration schematic of the cross-section of this resonator is shown in Figure 8 (b). The single crystalline (100) SiC film was produced by APCVD whereas the polycrystalline (111) SiC film by LPCVD. Both films were deposited on SiO₂/Si substrates. The experimental results showed that the 3C-SiC lateral resonators exhibit a resonant frequency similar to polysilicon devices and temperature coefficient of 22 ppm/ $^{\circ}\text{C}$ comparable to quartz oscillators (from 14 to 100 ppm/ $^{\circ}\text{C}$), which confirm the potential of SiC films for RF MEMS applications.

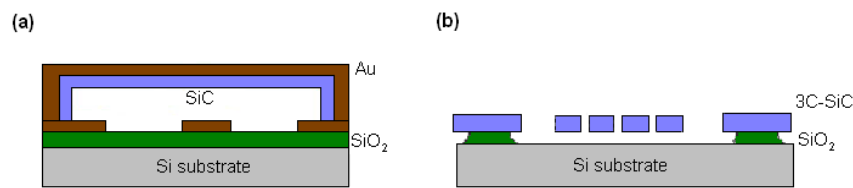


Figure 8. Examples of SiC thin film RF MEMS shown in the literature:

(a) switch and (b) lateral resonators.

5.3. BioMEMS

Biomedical or Biological Micro-Electro-Mechanical Systems (BioMEMS) are defined as systems or devices, which are constructed using micro/nanofabrication technology, for the analysis, delivery, processing, or for the development and construction of chemical and biological entities (Bashir, 2004). The first efforts in this field were directed to study the biocompatibility of common MEMS materials such as Si, SiO₂, Si₃N₄, polysilicon, SiC and SU-8. Kotzar et al. performed comparative studies among these materials and interesting conclusions were reached: (a) all materials were classified as non-irritants based on 1- and 12-week rabbit muscle implantations; (b) none of the materials were found to be cytotoxic in vitro using mouse fibroblasts; (c) only silicon nitride and SU-8 leached detectable non-volatile residues in aqueous physiochemical tests and (e) only SU-8 leached detectable non-volatile residues in isopropyl alcohol.

The biocompatibility of c-SiC and a-SiC films have been widely studied and promising results were reported (Santavirta, 1998; Kalnins, 2002; Coletti, 2007).

3C-SiC films grown on silicon substrates have been shown as a potential material for BioMEMS applications, especially for biosensing. Due to the mechanical strength, surface area-to-volume ratio, and extreme low mass, 3C-SiC BioMEMS structures have the potential to be mass sensors and resonators that are able to detect individual protein adsorption events (Zorman, 2012).

On the other hand, a-SiC based BioMEMS has been extensively developed and tested. Among the various bio-applications of a-SiC films can be mentioned: (i) coating material for implantable microsystems requiring hermetic sealing, owing to the fact that a-SiC is an excellent diffusion barrier material; (ii) membranes for microfluidics and Lab-on-a-Chip applications due to good a-SiC film chemical inertness property (Zorman, 2012).

6. Summary

In this chapter, the incorporation of dopant elements (such as N, P, B, Al and O) during the growth of SiC thin films has been described. The influence of each dopant type on the properties

of SiC films was discussed. Furthermore, the challenges and trends related to the SiC thin film technology for device applications were discussed. The literature has shown that a-SiC and c-SiC films have maintained the most relevant properties observed in different polytypes of SiC substrates. However, to obtain high quality films is necessary to optimize the growth conditions. This review has indicated that using low temperature growth processes and in situ doping are the trend to produce high quality SiC thin films compatible with microelectronic and MEMS technologies. Particular attention should be directed to grow large area uniform SiC films on Si and insulator/Si substrates, which is essential to make low-cost devices.

Regarding the SiC-based thin film applications, it was showed that these films have been widely used in electronic and MEMS devices such as diodes, TFTs, sensors, RF MEMS and BioMEMS. It is important to underline that the use of SiC films in the amorphous or crystalline form, doped or not, should be evaluated in terms of their properties. Much has been studied about the use of a-SiC films due to the fact of its ease of integration with the rising technologies, especially those that use temperature-sensitive substrates. Today, the area of bio-applications is a good example of this kind of requirement.

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