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Chemical vapor deposition of Si/SiC nano-multilayer thin films

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ABSTRACT

Stoichiometric SiC films were deposited with the commercially available single source precursor Et_3SiH by classical thermal chemical vapor deposition (CVD) as well as plasma-enhanced CVD at low temperatures in the absence of any other reactive gases. Temperature-variable deposition studies revealed that polycrystalline films containing different SiC polytypes with a Si to carbon ratio of close to 1:1 are formed at 1000 °C in thermal CVD process and below 100 °C in the plasma-enhanced CVD process. The plasma enhanced CVD process enables the reduction of residual stress in the deposited films and offers the deposition on temperature sensitive substrates in the future. In both deposition processes the film thickness can be controlled by variation of the process parameters such as the substrate temperature and the deposition time. The resulting material films were characterized with respect to their chemical composition and their crystallinity using scanning electron microscope, energy dispersive X-ray spectroscopy (XRD), atomic force microscopy, X-ray diffraction, grazing incidence X-ray diffraction, secondary ion mass spectrometry and Raman spectroscopy. Finally, Si/SiC multilayers of up to 10 individual layers of equal thickness (about 450 nm) were deposited at 1000 °C using Et_3SiH and SiH_4. The resulting multilayers features amorphous SiC films alternating with Si films, which feature larger crystals up to 300 nm size as measured by transmission electron microscopy as well as by XRD. XRD features three distinct peaks for Si(111), Si(220) and Si(311).

1. Introduction

Amorphous and crystalline Si/SiC multilayer films have been investigated due to their potential applications in thermal and mechanical coating technology [1,2], optoelectronics [3], telecommunication technology [4] and in cost-effective thin-film thermoelectric power generation devices [5,6,7]. The low thermal conductivity of these multilayers qualifies them as thermal barrier on devices operating at high temperatures [5]. Owing to the high wear resistance and the ability to oppress crack propagation, Si/SiC multilayers are used as protective layer on optical and electronic devices [5]. Furthermore, amorphous, hydrogenated Si/SiC multilayers are employed as photodiodes or photodetectors since they show excellent sensitivity and selectivity in the ultraviolet and visible spectrum [8,9,10]. Moreover, Si/SiC multilayers were used in thermoelectric power generators as an alternative to Si/SiGe quantum wells, which were used as n-type leg in general. Si/SiC quantum wells consisting of alternating Si and SiC thin films with a thickness of 100 nm show better conversion efficiency with increasing temperature [6], which results from the increasing Seebeck coefficient and the decreasing electrical resistance at elevated temperature [7]. Compared with Germanium, which is a rather rare material, silicon and carbon are abundant elements and thus a cost efficient alternative to classical thermoelectric materials.

Si/SiC multilayer films are usually deposited using dual source precursors. Silane or disilane are typically employed as silicon sources whereas hydrocarbons such as methane, propane or acetylene are used as carbon sources. De Cesare et al. used plasma enhanced chemical vapor deposition (PECVD) to synthesize amorphous and hydrated Si/SiC multilayers at temperatures between 140 and 300 °C with silane and methane as precursors [8,9,11]. Silane and propane are used in a rapid thermal chemical vapor deposition (RTCVD) process to deposit β-SiC heteroepitaxially on Si substrates at temperatures of 1200 °C with H_2 as reactive gas [12]. Myong et al. also utilized H_2 as reactive gas to deposit Si/SiC multilayers with silane and acetylene in a photo-CVD process [13,14]. Si/SiC multilayers with SiC and Si film thicknesses of 8 and 14 nm, respectively, were deposited by physical vapor deposition (sputtering) and the temperature dependent thermal conductivity of Si/SiC multilayers was determined [5].

In this paper, we present the deposition of SiC films with the commercial available single source precursor Et_3SiH. Two CVD processes (PECVD and thermal CVD) are used to deposit SiC films in order to compare the resulting film properties. The PECVD method allows the deposition of films at low temperatures. No other reactive gases are required to achieve the growth of stoichiometric, amorphous or crystalline SiC films. The influence of the substrate temperature on the growth

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process is demonstrated by measuring the growth rate and characterization of the film properties by XRD.

Thereby the film thickness was decreased without changing the film quality and the roughness of the deposited films was measured to be very low. Finally, the deposition of Si/SiC multilayers with a single source precursor is presented. Sequential deposition of Si and SiC films using SiH_4 and Et_3SiH at 1000 °C by thermal CVD process allowed the fabrication of a four-layer and a ten-layer structure which has high potential value for mechanical applications as well as for thermoelectric applications.

2. Experimental details

2.1. Thermal CVD

Thermal deposition experiments were performed in a custom-made cold-wall metalorganic chemical vapor deposition (MOCVD) reactor equipped with an inductively heated graphite susceptor, which allows a maximum temperature of the silicon substrate of up to 1200 °C. Three different organosilanes (Et_3SiH, Me_4Si, $PhSiH_3$) were investigated as single source precursors for the deposition of SiC material films in the temperature range from 900 to 1200 °C in the custom-made cold-wall reactor, from which Et_3SiH was identified as the most suitable single source precursor for the deposition of stoichiometric SiC films. Temperature-variable deposition studies revealed 1000 °C as the best substrate temperature for SiC film growth using Et_3SiH at a flow rate of 2 sccm. Polycrystalline films of cubic-type SiC with Si to carbon ratio of close to 1:1 were obtained under these deposition conditions. To avoid the formation of particles on the surface the precursor gas flow was diluted with an argon carrier gas. The dilution ratio of 1:80 emerged as the most effective.

2.2. Plasma CVD

PECVD studies were performed in order to deposit thin SiC films on silicon substrates at lower substrate temperatures and to compare the properties of the resulting SiC films with those obtained from the classical thermal MOCVD process. The silicon substrates were cut out of single crystalline <100> oriented Si wafers with a production tolerance of $+-0.5°$ and the surface was ultrasonically cleaned in acetone for 30 min prior to the deposition process. In order to compare the two deposition techniques in detail, the same precursor that was found to give the best results in thermal CVD (Et_3SiH) was used in the plasma process for the deposition of the SiC films. Since the precursor is decomposed in the plasma, the substrate temperature required for the PE-deposition of SiC thin films was expected to be lower compared to the thermal CVD process. A special plasma source was utilized to adjust the particle energies in the plasma giving the opportunity to investigate the influence of the plasma parameters on the resulting film properties in a wide range. The vacuum recipient is a gaseous electronics conference reference cell [15], which is equipped with a hybrid capacitive and inductive radio frequency (RF) plasma source (13.56 MHz). The plasma source features a special antenna design that provides the possibility to vary particle flow and particle energy independent of each other. Furthermore, energies can be set to very low levels (down to plasma energy). It consists of two electrodes with RF generators, which are used for inductive, capacitive, or a combined inductive–capacitive plasma excitation. A detailed description of the plasma source can be found elsewhere [16].

Argon diluted Et_3SiH was used as a process gas. Silicon substrates were placed on a heated substrate holder in the middle of the reactor and the substrate temperature was measured by a thermocouple. Deposition parameters such as deposition time, Et_3SiH concentration and substrate temperature were systematically varied to verify their influence on the resulting film properties.

2.3. Characterization

The film thickness was measured by profilometry (VEECO Dektak 6M) and ellipsometry (HORIBA MM-16-FGMS). The surface morphology of the resulting films was analyzed by scanning electron microscopy (SEM; Jeol JSM 6510) using operating voltage between 5 and 15 kV. Cross section samples were prepared with the Jeol Cross-Section Polisher (Jeol IB-09010CP) and measured with an operating voltage of up to 25 kV. In addition, AFM (Veeco Dimension 3100) measurements in contact mode were performed to measure the surface roughness of the deposited films.

The chemical composition was analyzed by energy-dispersive X-ray analysis (EDX, Bruker Quantax 400, acceleration voltage 10 kV, counting time 160 s.). The system was calibrated using a crystalline SiC film as standard. Additionally secondary ion mass spectroscopy (SIMS) measurements were used to measure the stoichiometry of the obtained films as a function of the film thickness. SIMS of positive and negative ions was performed in a LEYBOLD LHS 10 system with a secondary ion and neutral mass spectrometer module (SSM 200) using a Balzers 511 quadrupole for mass separation. The base pressure in the analysis chamber is about $5*10^{-10}$ mbar. For sputter erosion, the samples were bombarded by a scanned focussed 5 keV Ar^+ ion beam of about 1 μA under an angle of 60° to the surface normal. For the presented depth profiles, the ion beam with a FWHM of about 100 μm was scanned over an area of 3 mm × 2 mm. To increase depth resolution, sputtered particles from the crater walls are suppressed by electronic gating.

The crystallinity of the deposited films was investigated by X-ray powder diffraction measurements (XRD) as well as by grazing incidence X-ray diffraction (GIXRD, Panalytical Empyrean, MoKα radiation = 0.7107 Å).

Transmission electron microscope (TEM) investigations of a four-layer Si/SiC-system deposited on a SiC substrate were conducted in a TEM FEI-Philips CM300 UT/FEG, operated at 300 kV, equipped with a Gatan CCD for image recording and with a Thermo NSS system for Energy Dispersive X-ray Spectrometry (EDS) analysis (Ge-detector). The cross section sample was prepared by the face-to-face technique and finally by dimple grinding and ion beam etching [17].

Raman Spectroscopy (Horiba-Jobin Yvon, Labram, 514 nm Argon laser) was used to characterize the deposited films and to identify the SiC polytype in the material.

3. Results and discussion

3.1. SiC film growth by thermal CVD

Preliminary tests revealed Et_3SiH as the most suitable single source precursor for the thermal CVD deposition of stoichiometric SiC films at a temperature of 1000 °C in respect to the resulting composition (Si:C molar ration) and crystallinity. An “inverse” reactor geometry, in which the precursor gas was introduced from the bottom and the substrate was placed at the upper part of the reactor, was applied in order to prevent the deposition of particles on the surface from parasitic gas phase reactions (decomposition reactions) of the precursor. In addition, the precursor gas flow was diluted with argon carrier gas as the precursor concentration was found to have a strong influence on the particle formation. Four different dilution ratios with continuously increasing argon concentration (1:10, 1:20, 1:40 and 1:80), which was controlled by mass flow controllers, were examined. The tendency of particle formation could clearly be reduced with increasing dilution ratio and thus decreasing Et_3SiH concentration indicating reduced gas-phase reaction activity. At the same time, the deposition rate is reduced with higher dilution ratio. Hence, the chosen dilution ratio of 1:80 in the following deposition processes is a compromise to reduce particle formation while having a sufficient deposition rate. Furthermore, the effect of deposition time on the morphology and thickness of the SiC film