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Article

Characterization of $Si_{1-x}C_x$:H Thin Films Deposited by PECVD for SiCOI Heterojuntion Fabrication

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As heterojunções de SiC em isolante, conhecidas como SiCOI (SiC-on-insulator), ao combinar as vantagens do SiC e do substrato de Si mostram-se interessantes para aplicações em altas temperaturas, alta potência, altas freqüências, sensores inteligentes, e aplicações micro-mecânicas. Neste trabalho pesquisamos as propriedades de filmes finos de carbeto de silício amorfo hidrogenado (a-$Si_{1-x}C_x$:H) depositado por PECVD em substratos de silício e silício coberto por uma camada isolante, antes e após o recozimento térmico para a cristalização do filme. Devido a seu grande interesse em aplicações optoeletrônicas foram pesquisadas quatro tipos de isolantes diferentes: SiO_2 térmico obtido a altas temperaturas (1100 °C), SiO_2, SiO_xN_y, e Si_3N_4 obtidos por PECVD a baixa temperatura (320 °C). A análise de infravermelho nas amostras como depositadas mostra que o filme depositado em substrato de silício coberto por Si_3N_4 possui uma melhor coordenação entre os átomos de Si e C. O recozimento térmico realizado conduz à cristalização de todos os filmes amorfos depositados. As medidas Raman exibem a vibração referente ao C-C somente para os filmes depositados sobre isolantes PECVD, depois de recozidos. Os resultados da análise de DRX mostram que os filmes depositados em substrato de Si(100) e Si(100) coberto com SiO_2 térmico apresentam orientação cristalina preferencial na direção (100), enquanto os filmes depositados em substrato de silício coberto com isolantes PECVD apresentam uma banda larga associada com a difração do H-SiC(10L) e do 3C-SiC(111).

The SiC-on-insulator (SiCOI) heterojuntion is interesting for high temperature, high power, high frequency, smart-sensors, and micromechanical applications, due to the combined SiC and Si substrate advantages. In this work we investigate the properties of amorphous hydrogenated silicon carbide thin films (a-$Si_{1-x}C_x$:H) deposited by PECVD onto silicon and silicon covered with an insulator layer, before and after thermal annealing processing aiming crystallization of the deposited films. Due to their great interest for optoelectronic applications, four different insulator materials are investigated: high temperature (1100 °C) thermal SiO_2, low temperature (320 °C) PECVD SiO_2, SiO_xN_y, and Si_3N_4. The infrared absorption studies for as-deposited films show that films grown onto silicon covered with Si_3N_4 layer have a better coordination among Si and C atoms. Post-growth thermal annealing leads to the crystallization of the material for all the studied amorphous films. Raman measurements exhibited C-C bond vibration bands, after annealing, only for films deposited onto PECVD insulator. XRD results showed that films deposited on thermal-SiO_2/Si(100) and Si(100) substrates have also a preferential (100) crystalline orientation, while films deposited on PECVD-insulator/Si(100) present a broad band associated with H-SiC(10L) and 3C-SiC(111) diffractions.

Keywords: silicon carbide, PECVD, infrared spectroscopy, Raman spectroscopy, X-ray diffraction

Introduction

In recent years, silicon carbide (SiC) has received considerable attention, due to the possibility of obtaining materials with a variety of topological structures, which affect the electronic density of states and the optical properties.[1] Indeed, beyond its good thermal stability and mechanical hardness, this material is versatile from structural considerations, electronic behavior as well as the photoluminescent response.[2, 3]

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SiC, either in its amorphous or crystalline forms has been the subject of intensive investigation for several applications in the optoelectronic and microelectronic field such as, thin film light emitting diodes,[4] electroluminescent devices,[5] and heterojuntion bipolar transistors.[4,6] Crystalline SiC is a prospective material for electronic devices. Its fundamental properties such as large band gap, high thermal conductivity, high electrical breakdown field strength, and high saturation drift velocity make it a suitable material for high power, high temperature and high frequency devices.[1,7]

At the same time, SiC grown on silicon, allows the integration of the high temperature capabilities of SiC with the electronic and micromachining possibilities of Si. However at temperatures higher than 500 K the SiC/Si heterojunction starts leaking, resulting in current flow through the Si substrate. One method to avoid this problem is the deposition of SiC on SOI (silicon on insulator) substrates in order to obtain SiC-on-insulator (SiCOI) structures. These structures are desirable not only for low-cost, large-area substrates for high temperature and optoelectronic applications but also for high power, high frequency, smart-sensors, micro-mechanical devices that must operate in chemically and/or physically aggressive environments, at high temperature and at high radiation ranges.[8,9]

Various growth methods have been developed and applied to prepare high quality SiC films. Plasma-enhanced chemical vapor deposition (PECVD) is understood to be a versatile and well-established technology. This technique offers the possibility of utilizing low temperature; designing new structures and changing the properties associated with films micro-structure through the change of technological parameters. It also permits the growth of large-area films.[10]

In this paper we investigate the characteristics of SiC obtained by high temperature annealing of amorphous hydrogenated silicon carbide a-$Si_{1-x}C_x$:H films deposited by PECVD on silicon and silicon covered with an insulator layer substrates. We analyze different kinds of insulator capping layers chosen due to their great interest for optoelectronic and microelectronic applications.

Experimental

The SiCOI heterojuntions were prepared on <100> oriented p-type Czochralski silicon, with average resistivity in the 8-12 Wcm range. First, the insulator films were grown on the Si substrate followed by the a-$Si_{1-x}C_x$:H films deposition. All a-$Si_{1-x}C_x$:H films were deposited by PECVD from CH_4(32.4 sccm) and SiH_4(3.6 sccm) mixtures, with H_2 dilution in the "starving plasma regime" at 300 °C with a power of 100 W. A parallel-plate radio frequency (RF, 13.56 MHz) PECVD reactor was utilized.

The PECVD insulator capping layers were deposited from: SiH_4(15 sccm) and N_2O(75 sccm) mixtures, at 320 °C, with a power of 200 W for the SiO_2, SiH_4(15 sccm) and N_2O(37.5 sccm) mixtures, at 320 °C, with a power of 200 W for the SiO_xN_y, and SiH_4(3 sccm) and N_2(39 sccm) mixtures, at 320 °C, with a power of 100 W for the Si_3N_4. The thermal SiO_2 films were grown by dry oxidation at 1100 °C for 2 h 30 min.

Thermal annealing processing, at 1200 °C for 2 h under nitrogen flow, was performed in order to improve the atomic structure of the amorphous films and induce crystallization. The chemical bonding in the films, before and after thermal annealing, are investigated by Raman scattering with excitation provided by a He-Ne red laser operating at a wavelength of 633 nm, and by Fourier transform infrared spectrometry (FTIR) using a *BioRad* FTS 40 Fourier transform infrared spectrometer with a resolution of 8 cm^{-1} in the 400–4000 cm^{-1} wave number range. Either silicon or silicon covered with the concerned insulator capping layer substrates were used as references in both cases. The structural properties are studied by X-ray diffraction (XRD). These measurements were performed by a *URD-6 GmbH* diffraction system in the θ-2θ scan configuration utilizing the Cu $K\alpha$ wavelength of 1.5418 Å.

Results and Discussion

FTIR analysis

Figure 1 shows the IR spectra for as-deposited films. This Figure reveals the absorption band attributed to Si-C stretching mode centered at 779 cm^{-1} for all the films, except for film deposited onto Si covered with Si_3N_4 where the band is centered at 783 cm^{-1}. Other peak observed at ~1000 cm^{-1} is generally assigned to SiC-H_n modes; however, as no traces of other C-H_n bonds vibration modes are observed we believe that this peak is doe to some kind of Si-C vibration mode. In addition, a peak at 2100 cm^{-1}, related to Si-Hn stretching vibrations, is observed. The position, the larger area and the sharp increase of the Si-C related band, observed for the film deposited onto Si covered with Si_3N_4 indicate that this film presents a better coordination among Si and C atoms. Carefully inspecting Figure 1, we can also observe that films deposited in these conditions do not present C-H_n bonds.

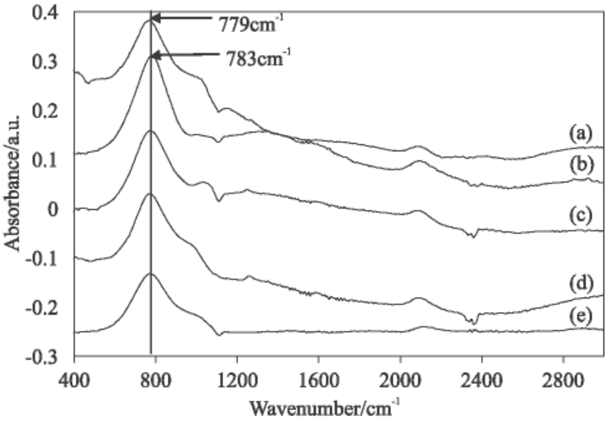

Figure 1. Infrared spectra for as-deposited films, (a) $SiC/Si_3N_4/Si$, (b) SiC/SiO_2-Thermal/Si, (c) $SiC/SiO_xN_y/Si$, (d) SiC/SiO_2-PECVD/Si and (e) SiC/Si.

After annealing all the spectra exhibit a shift of the Si-C peak position towards 798 cm^{-1}, a decrease in peak width and a change in line shape, as can be seen in Figure 2. The line shape of the Si-C related band, in the infrared spectra, for as-deposited films is of Gaussian type and after thermal annealing at 1200 °C it changes to Lorentzian type. This change in line shape as well as the decrease in peak width indicates the onset of crystallization. The observed change in line shape after annealing is consistent with a more uniform environment of the Si–C bond and further evidence of structural modification is given by the decrease in bandwidth, indicating increasing structural order due to the formation of microcrystallites. The peak shift is due to the reduction of Si–C bond length resulting in an increase of the effective force constant.[10]

The peaks corresponding to $Si-H_n$ (~2100 cm^{-1}) bonds disappear after thermal annealing, indicating that these treatments cause the total hydrogen outdiffusion from the film together with crystallization. The other peaks observed are (400 to 500 cm^{-1} and 1000 to 1300 cm^{-1}) related to the insulator capping layer. The negative peaks are associated with difference between the insulator capping layer substrate and the reference thickness as well as with the sputtering of the insulator capping layer at the beginning of the a-$Si_{1-x}C_x$:H deposition due to the hydrogen plasma predominance.

The FTIR data analysis on Figures 1 and 2 are compatible with our previous reports indicating lower H incorporation and higher chemical and structural order, for a-$Si_{1-x}C_x$:H films grown under "starving plasma regime" and H_2 dilution conditions.[11,12] The results showed better material quality when compared with works reported by Jung *et al.*,[13] where no H_2 dilution was used, which showed considerable $C-H_n$ and $Si-H_n$ bonds before and after thermal annealing.

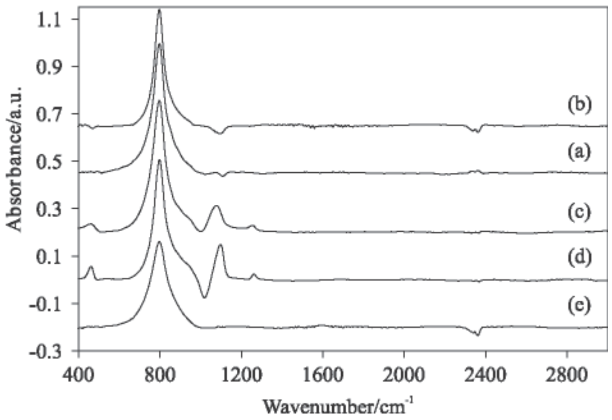

Figure 2. Infrared spectra for films after annealing at 1200 °C for 2 h, (a) $SiC/Si_3N_4/Si$, (b) SiC/SiO_2-Thermal/Si, (c) $SiC/SiO_xN_y/Si$, (d) SiC/SiO_2-PECVD/Si and (e) SiC/Si.

Raman analysis

In Figure 3 the Raman spectra for the as-deposited films are shown. All the films reveal the second-order band related to crystalline silicon, located at 925-1060 cm^{-1} and there are not evidences of any band or peak corresponding to C-C or a-Si-Si bonds.

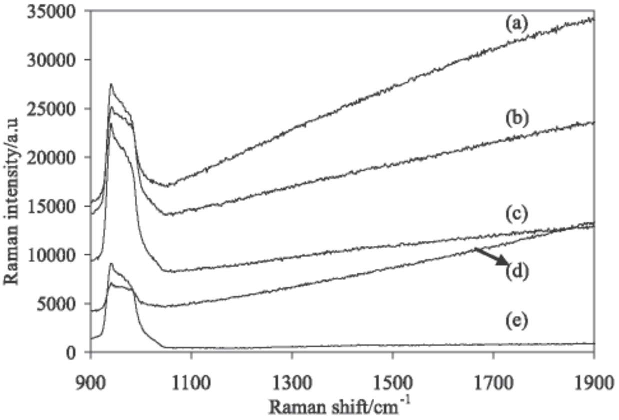

Figure 3. Raman scattering spectra from films as-deposited, (a) $SiC/Si_3N_4/Si$, (b) SiC/SiO_2-PECVD/Si, (c) $SiC/SiO_xN_y/Si$, (d) SiC/SiO_2-Thermal/Si and (e) SiC/Si.

Raman measurements after the annealing steps are depicted in Figure 4. Films deposited onto bare Si and thermal-SiO_2/Si do not present any C-C related band or peak. Giving evidences that films are understoichiometric configuration and thus all the carbon atoms are "used" to form silicon carbide. Spectra measured for films deposited on PECVD insulator/Si, after annealing, show a weak C-C signal splited into two subbands at ~1330 cm^{-1} and ~1595 cm^{-1}, corresponding to D line (disordered) and G line (graphite) respectively. For films deposited onto SiO_xN_y/Si, the C-C signal is larger. In all cases the spectra show the second-order band of crystalline silicon, located at 925-1060 cm^{-1}.

However, no peaks directly related to Si-C for films neither as deposited nor annealed are observed. In this case the TO peak from crystalline 3C-SiC at 796 cm^{-1} does not appear because it is aligned with the Si substrate and the measurements are made in backscattering geometry; also the LO peak at 972 cm^{-1} is probably superimposed to the second-order band of crystalline silicon, located at 925-1060 cm^{-1}.

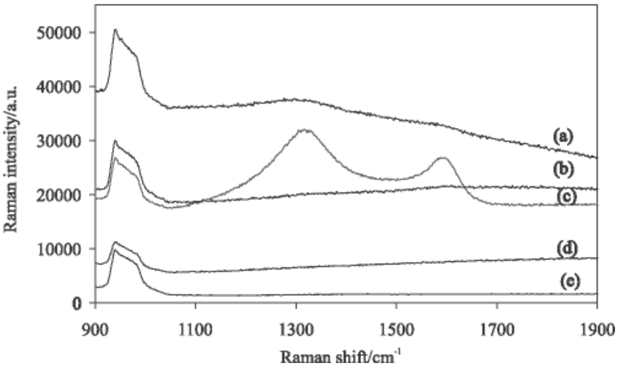

Figure 4. Raman scattering spectra from films after thermal annealing at 1200 °C for 2 h, (a) SiC/Si$_3$N$_4$/Si, (b) SiC/SiO$_2$-PECVD/Si, (c) SiC/SiO$_x$N$_y$/Si, (d) SiC/SiO$_2$-Thermal/Si and (e) SiC/Si.

XRD analysis

Figure 5 shows the X-ray diffractograms for the annealed films. It can be observed, in agreement with FTIR results, that the post-deposition thermal annealing leads to the crystallization of all the amorphous films. Films deposited onto bare Si(100) and onto thermal-SiO$_2$/Si(100) substrates exhibit an intense diffraction peak at ~41° corresponding to 3C-SiC(200) diffraction, indicating a preferential orientation in the (100) crystalline direction. This peak is more pronounced for films deposited onto thermal-SiO$_2$/Si(100).

Films deposited onto PECVD insulator/Si(100) exhibit one peak at ~33° related to the crystalline Si(200) diffraction and an additional broad band associated with H-SiC(10L) and 3C-SiC(111) diffractions.

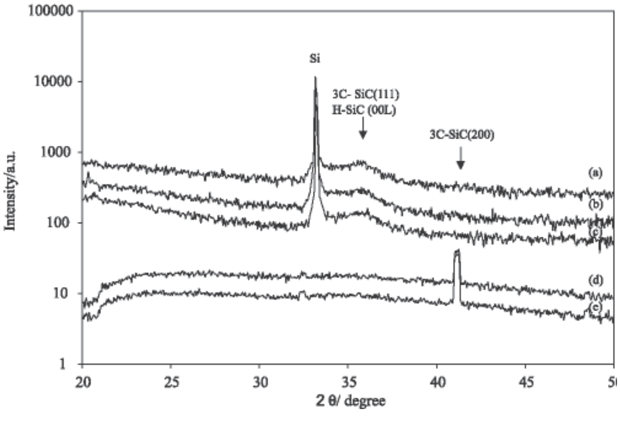

Figure 5. X-ray diffractograms for films after thermal annealing at 1200 °C for 2 h, (a) SiC/Si$_3$N$_4$/Si, (b) SiC/SiO$_x$N$_y$/Si, (c) SiC/SiO$_2$-PECVD/Si, (d) SiC/Si and (e) SiC/SiO$_2$-Thermal/Si.

Conclusions

In summary, using a PECVD reactor we have obtained SiC/Si and SiCOI structures with different characteristics. The FTIR analysis for as-deposited films shows that films deposited on silicon covered with Si$_3$N$_4$ layer have a better coordination among Si and C atoms. The FTIR and XRD analysis show that post-deposition thermal annealing leads to the crystallization of all amorphous films.

Raman measurements indicated that films deposited on PECVD-insulator/Si substrates, after annealing, present a weak signal related to C-C bond vibrations, this C-C signal being larger for film deposited onto SiO$_x$N$_y$/Si.

We observed preferential (100) crystalline orientation of SiC deposited on bare Si(100) and thermal-SiO$_2$/Si(100) substrates, being more pronounced for the film deposited on thermal-SiO$_2$/Si(100) substrate. For films deposited on PECVD insulator/Si(100), diffraction bands related to H-SiC(10L) and 3C-SiC(111) were detected after the annealing process.

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