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VACUUM ANNEALING OF PECVD SI-RICH, A-SIC: H THIN FILMS WITH VARYING STOICHIOMETRY FOR HIGH TEMPERATURE MEMS-NEMS APPLICATION

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Abstract- SiC is an excellent structural material for harsh environmental MEMS and NEMS applications due to its outstanding mechanical, thermal properties, high hardness ,low friction coefficient and high wear resistance. It can be a direct replacement to Si-based micro-fabrication technology because of its extreme chemical inertness, extremely hard micromachinable capability than any other materials like Si, AlN etc. Amorphous hydrogenated Silicon rich Silicon Carbide thin films grown were prepared by low temperature plasma enhanced chemical vapour deposition on Si-Substrate by using a mixture of Silane and Methane as precursor and Argon as carrier gas by varying gas flow ratio, RF-power, working pressure and with a deposition temperature of 400°C. After deposition, subsequently rapid thermal annealing was carried out at 450,650, and 850 °C at vacuum level of 10^{-3}Torr. Due to annealing, the film's densification occurs and internal stresses are generated due which formation of cracks on the film occurs during annealing. The as-deposited and annealed SiC thin films were investigated by Optical microscopy, Scanning Electron Microscopy, Grazing Incidence X-ray Diffraction and Raman spectroscopy (532nm Wave length) techniques. For higher annealing temperatures, formation of short range ordering of nanocrystals (NCs) Si was observed in a:SiC-H thin films by Raman spectroscopy and GIXRD. The difference in the thermal expansion coefficient of Si and SiC has contributed to cracking of a:SiC-H thin films which was observed by optical microscopy and Scanning electron microscopy images.

Keywords: PECVD, GIXRD, Nanocrystals

1. INTRODUCTION

Vacuum Annealing of Si-rich,amorphous hydrogenated Silicon Carbide (a-$Si_{1-x}C_x$:H) thin films prepared by plasma enhance chemical vapour deposition (PECVD) has attracted great interest in the field of photovoltaics,optoelectronics and MEMS –NEMS sensors[1]high temperature protective coatings[1],excellent passivation layer material for silicon solarcells[2].Using the multilayer approach proposed by Zacharias [3], it's possible to generate Si nanocrystals through annealing of a-Si1-xCx:H thin films.However,for multilayer film crystallisation temperature depends on the amount of Si in the a:SiC-H thin films,the size and the nanocrystaldensity can be controlled by a stoichiometric Si diffusion barrier layer and the composition of Si-rich multilayers[4]. The differences in thermal expansion coefficient of Si and SiC has contributed to cracking of films. [5]

In this present work the widely used method for the deposition of a-SiC:H layers by decomposition of Silane(SiH_4) and Methane(CH_4) as a precursors and Argon (Ar) as a carrier gas PECVD with near stoichiometric ratio with optimised deposition parameters (i.e. RF Power and flow ratio the gases) to get higher growth rate. The microstructural investigation of the thin films was done showing that they are strongly dependent on deposition conditions. The structural studies during thermal annealing of PECVD a-SiC:H thin films were investigated, during the vacuum thermal annealing at 450,650 and 850 °C the crystallisation of Si and SiC NC'S in Si-rich a:SiC-H thin films was observed by Surface Enhanced Raman spectroscopyand the formation of crystalline phases was investigated by Grazing incidence X-ray diffraction. The Si-rich, a-SiC:H thin films during rapid thermal annealing internal stress are induced which leads to the formation of cracks on the films.

2. EXPERIMENTAL DETAILS

In this present work the Structural investigation was carried out with GIXRD(Grazing Infrared X-Ray Diffraction)and Micro Raman Spectroscopy(532nm) which had detected the nanocrystalline phase formation during thermal annealing process (RTA) at 450, 650 and 850 °C.

Amorphous hydrogenated Si-rich (a-$Si_{1-x}C_x$:H) multilayer films were deposited at 400°C with high frequency source 13.56 MHz . For deposition of samples we used a power density. The precursor gases SiH_4, CH_4 and Argon were used to deposit the a-$Si_{1-x}C_x$:H:H on n-type(100) Si-substrate. Table 2.1 shows the deposition

parameters. After deposition of the films,a thermal annealing was performed at different temperatures (450,650, 850°C) holding time 10 min under vacuum atmosphere 10^{-3}Torr.A heating rate of 25 °C/min and cooling rate 100 °C/min was applied. Due to thermal annealing the changes in the morphology was observed by optical microscopy and Scanning electron microscopy and formation of cracks on the films.

Micro Raman Spectroscopy was done using a laser operating at an excitation wavelength of nm and a 100X optical microscope object lens. Raman measurements were carried out on Si-substrate to avoid supplemental raman bands from the substrate. The short range ordering of nanocrystal Si was observed in the amorphous matrix films (a-$Si_{1-x}C_x$:H) with increasing annealing temperatures.

For Grazing Incidence X-Ray Diffraction (BRUKER D8 ADVANCE) was used for investigation of the formation of crystalline phase during annealing process.

Table-2.1 Shows the Deposition Parameters

Film	**Temperature °C**	**Pressure mTorr**	**RF power Watts**	**Gas flow ratio sccm $SiH_4/CH_4/Ar$**
a:SiC-H	1400	400	400	8/100/700

3. RESULTS AND DISCUSSION

3.1 Optical Microscopy

Fig. 3.1.(a,b,c) shows that optical microscopy images of Amorphous hydrogenated silicon carbide (a-$Si_{1-x}C_x$:H)) thin films which were characterized for as-deposited and after thermal annealing them (450,650,850°C) by using Olympus optical microscopy GX-51. The images were taken at magnification of 1000X for investigation of cracks formation on the films.

Fig. 3.1Optical Images of a:SiC-H thin films (a) Annealed at 450 ºC(b) Annealed at 650 ºC (C) Annealed at 850 ºC

3.1 Scanning Electron Microscopy

Fig. 3.2.(a,b,c) shows the SEM images were taken at acceleration voltage 15kV and working distance 15mm for as-deposited and annealed (a-$Si_{1-x}C_x$:H) thin films.

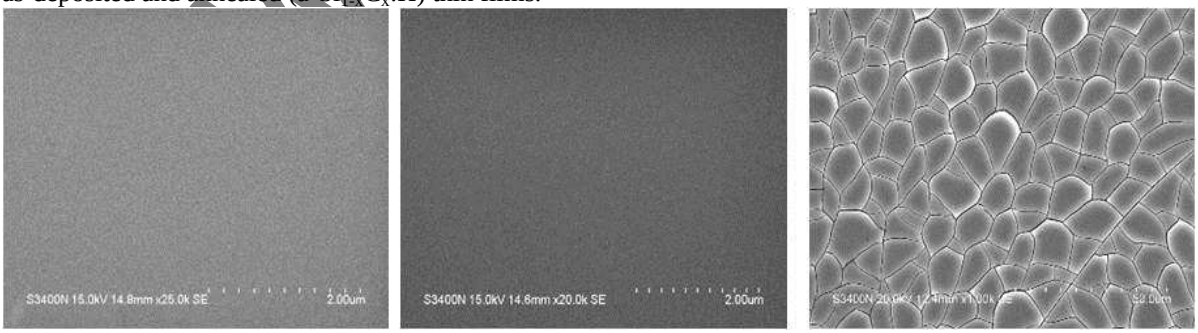

Fig. 3.2 SEM Images of a:SiC-H thin films (a) Annealed at 450 ºC (b) Annealed at 650 ºC(c) Annealed at 850ºC

3.2 Structural Transformation During Annealing

3.2.1 Micro Raman Spectroscopy

In this work, Raman spectroscopy is used to probe the transition from amorphous to crystalline and to quantify the amorphous and crystalline fraction of Si in as-deposit and annealed a-$Si_{1-x}C_x$:Hthin film. It was experimentally and theoretically shown that the peak frequency of the Raman active mode of Si is shifted to lower frequencies when the crystallite size increases. Fig. 3.3 shows the transformation of Si bonds within thea-$Si_{1-x}C_x$:H thin film with increasing annealing temperature. In the Raman spectra of the as-deposited and

annealed samples, the bonding structure is dominated by small nanocrystals~520 cm $^{-1}$ Silicon due to Si-substrate peak[6].The peaks around 950cm $^{-1}$ belongs to Si-C LO (Longitudinal Optic)phonon vibration[7] and the peak from 1400 to 1470 cm $^{-1}$ are due to disordered graphitic like carbon sp^2 bonded D band[8-9]

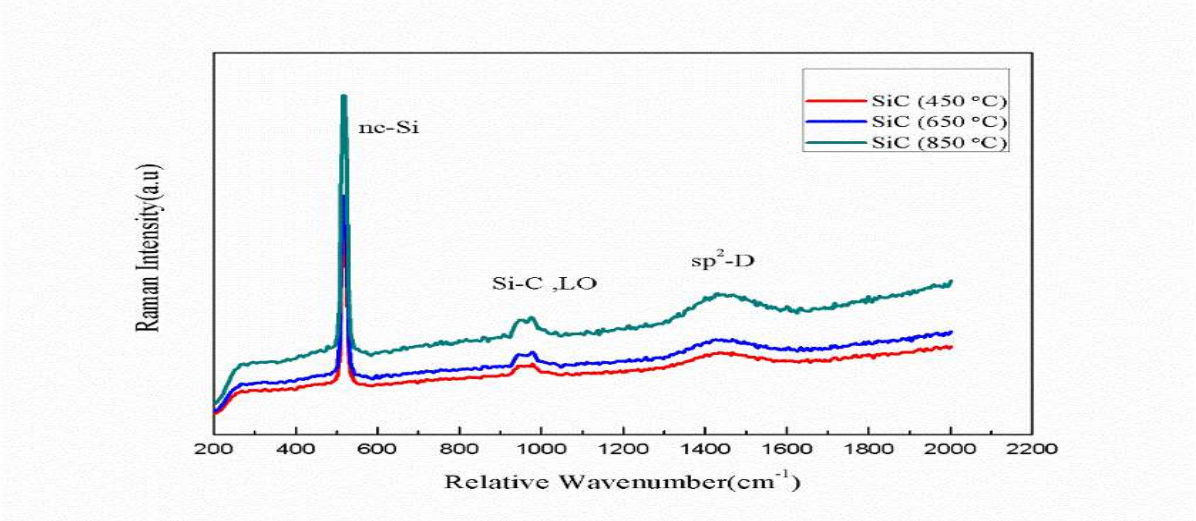

Fig. 3.3 Raman Spectra of Si Cannealed at Temperature (450, 650, 850 °C)

3.3 Grazing Incidence X-Ray Diffraction

The formation of crystalline phases during annealing was investigated by GIXRD.
In Fig 3.3, XRD pattern of a SI-rich SiC thin film annealed at different temperature are shown. The a-$Si_{1-x}C_x$: Hthin film remains amorphous after annealing at 450ºC. In contrast, when the a-$Si_{1-x}C_x$:H films are annealed at 650ºC for 10 min.A broad Bragg reflection around 28.5 occurs which is attributed to the (111) lattice plane of crystalline Si. In addition, a broad hump occurs at 53 and 53.5º,2θ due to onset of Si crystallisation due to (200), (220) lattice planes of SiC.

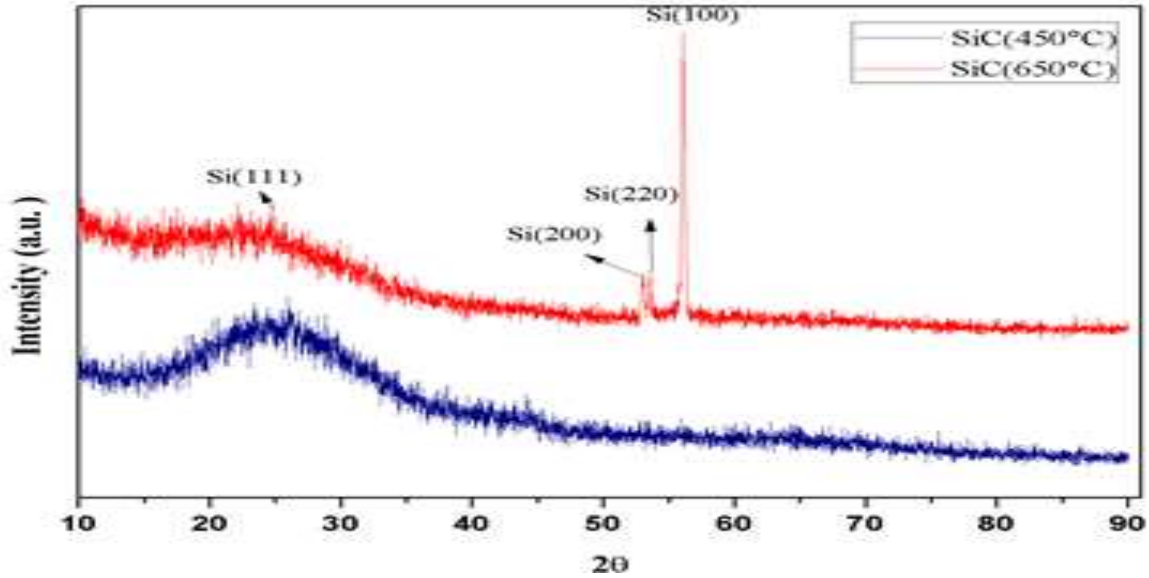

Fig. 3.4 XRD Pattern of SiC Annealed at Temperature (450,650,850 °C)

The crystalline domain size L were calculated from the peak width according to Scherrer's formula. [10]

$$L = \frac{K\lambda}{B(2\theta).cos\theta}$$

B (2θ) is the full width in radians,corrected for the instrumental contribution,subtended by half maximum intensity width of the appropriate diffraction pattern peak. For the geometrical factor k, a value of 0.9 was chosen for Si and SiC[11]. The domain size of Si NC's size was estimated ~2 nm when the annealing temperature was 650ºC.

CONCLUSIONS

In this study the annealing affect of a-$Si_{1-x}C_x$:H thin film deposited by PECVD was investigated directly after deposition samples were amorphous. When the annealing exceeds 650 ºC,Si crystallises NCs size was estimated ~2 nm by GIXRD. The Raman band at ~520cm $^{-1}$ is due to Si-substrate peak and small nanocrystals Si .The

peaks around 950cm $^{-1}$ belongs to Si-C LO (Longitudinal Optic)phonon vibration and the peak from 1400 to 1470 cm $^{-1}$ are due to disordered graphitic like carbon. Due to thermal annealing, the changes in the surface morphology was observed by optical microscopy and Scanning electron microscopy and formation of cracks on the films.

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