Indian J. Phys. 77A (5), 433-439 (2003)

AN INTERNATIONAL JOURNAL
IJPA

Microcrystallization and/or columnar growth at Si:H network induced by Ar dilution to the SiH_4 plasma in rf glow discharge

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Received 3 March 2003, accepted 30 April 2003

Abstract : In quest of an alternative to H_2 dilution for rapid microcrystallization, the effect on the Si:H film properties has been studied for Ar dilution to the SiH_4 plasma over an extremely wide range from $d(Ar)$ = Ar/SiH_4 = 60 to 1200. It is demonstrated that Ar dilution in SiH_4 plasma induces crystallization in Si:H at a low rf power. It is proposed that Ar* in Ar-diluted plasma plays an analogous role for initiating microcrystallization, as atomic H does in H_2-diluted plasma. However, extremely high Ar dilution induces a heterogeneous network and leads to columnar structure.

Keywords : Ar dilution, microcrystallization, PVD-like growth, structural heterogeneity, columnar structure.

PACS Nos : 81.05.Gc, 81.05.Rm, 81.15.Gh

1. Introduction

Very high hydrogen dilution is the most tricky parameter among a few others like high electrical power applied to the electrodes, moderately high substrate temperature and gas pressure in the deposition chamber, that facilitate the growth of hydrogenated microcrystalline silicon (μc-Si:H) films when prepared from SiH_4 plasma in rf glow discharge. Matsuda [1] proposed the surface reaction model and demonstrated that higher hydrogen dilution induces microcrystallization in the Si:H by increasing the diffusion length of favourable Si precursors at the growing Si network. Veprek [2] and Tsai *et al* [3] proposed that hydrogen controls the microcrystallization process by promoting etching of the loosely bonded network at the film surface and maintaining chemical equilibrium. Asano [4] reported that the structure of Si:H films could be changed from amorphous to microcrystalline phase by alternating the process of film deposition and exposure to H_2 plasma. However, no significant etching of the deposited film was observed and it was proposed that macroscopic etching is not essential for microcrystallization. Extended hydrogen plasma exposure, during growth interruption, on stacked layer Si:H films demonstrated quantum confinement effects and the growth of silicon nano-structures [5]. Shimizu proposed the chemical annealing [6,7] by atomic H at the growth zone as a powerful tool to mobilize the network structure that could initiate nucleation and grain growth at the Si matrix.

In quest of some other gas, in place of H_2, as diluent for SiH_4, it has been identified that Xe dilution reduces the light induced degradation [8], Ar dilution induces the crystallization process [9] and, in general, noble gas dilution increases the deposition rate [10,11]. With a view to attaining a rapid microcrystallization process and a high growth rate for the film deposition, we have studied the effect of Ar dilution to the SiH_4 plasma, over an extremely wide range and the corresponding changes on the optical, electrical as well as the structural properties of the Si:H network have been reported in the present paper.

2. Experimental

The Si:H films were prepared in a capacitively coupled rf (13.56 MHz) glow discharge system at a substrate temperature of 180°C, from (SiH_4 + Ar)-plasma activated by

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contained a dense patch with black contrast, which was supposed to be Si crystallite. The μc-Si grains of diameter

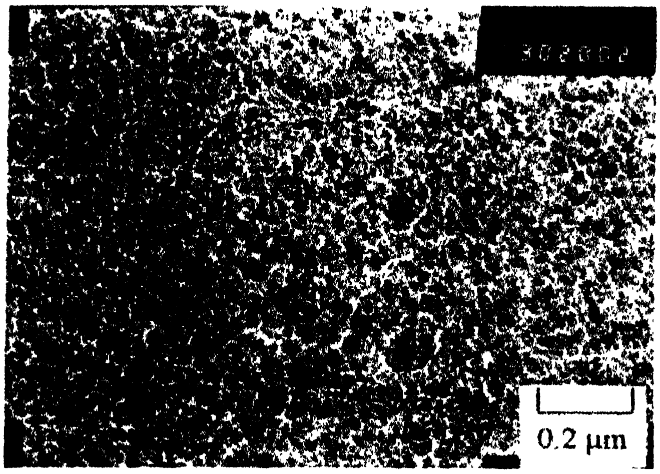
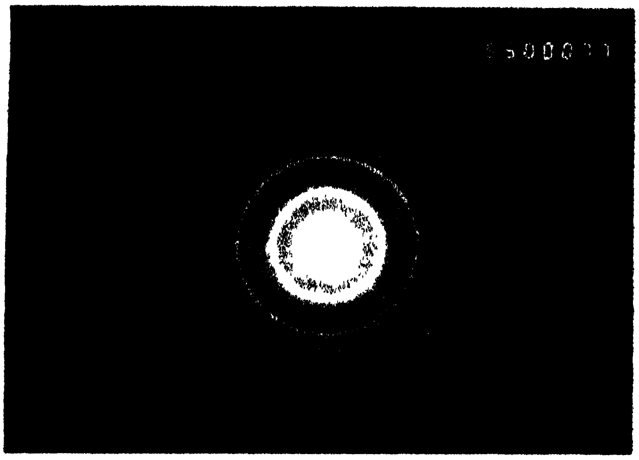


Figure 6(a) TEM micrograph for μc-Si H films prepared at Φ(Ar) 200.

~100–350 Å were observed in the micrograph. The associated electron diffraction pattern as shown in Figure 6(b), identified sharp crystallographic rings



Figrue 6(b). Electron diffraction pattern, for μc-Si:H films prepared at Φ(Ar) = 200.

corresponding to (111) (220) (311) planes of *c*–Si. The TEM features suggested the columnar aggregation composed of longitudinally associated μc-Si grains with irregular shapes. The connecting areas in between the columns indicated by white contrast (in the micrograph) were likely to be the amorphous connecting tissues associated to columnar growth morphology. However, the nucleation process was hindered in the presence of very high Ar dilution. The μc-Si grains were almost absent over the similar basic matrix in the TEM micrograph (Figure 7(a)) for the film prepared at Φ(Ar) = 800 and the corresponding halo-like diffraction pattern (Figure 7(b)) demonstrated an amorphous network structure all over the island and tissue areas.

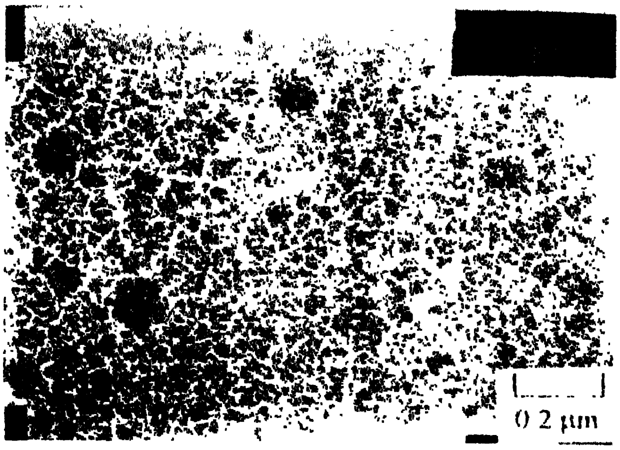


Figure 7(a). TEM micrograph for Si:H films prepared at Φ(Ar) = 800

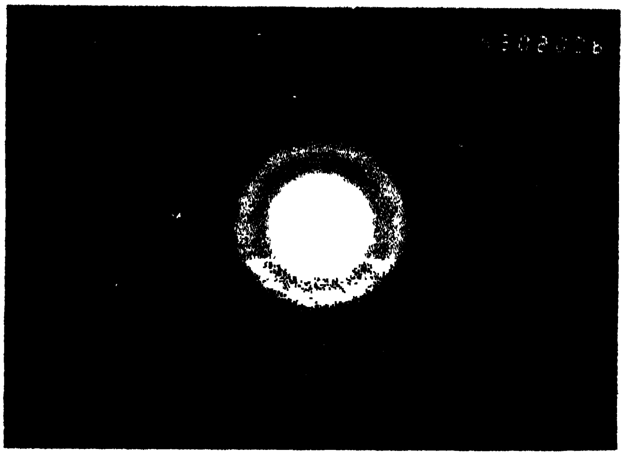


Figure 7(b). Electron diffraction pattern, for Si:H films prepared at Φ(Ar) = 800

3.5. Scanning electron microscope studies :

Scanning electron microscope (SEM) studies revealed a number of blisters on the surface of the films prepared

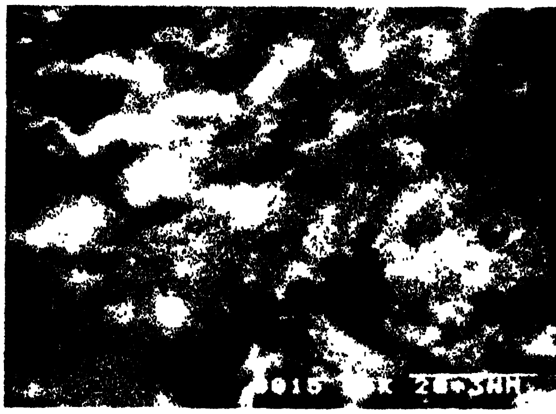


Figure 8(a). SEM micrograph revealing the surface roughness on the Si:H films prepared at Φ(Ar) = 1200.

at Φ(Ar) ≥ 400 and the surface was roughened vigorously at an extremely high Ar dilution at Φ(Ar) = 1200 (Figure 8(a)). The SEM micrograph (Figure 8(b)) at the

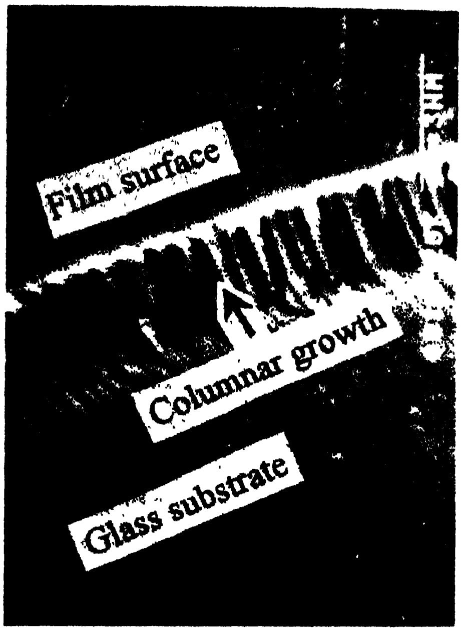


Figure 8(b). SEM micrograph at the fracture surface demonstrating the columnar growth at the Si:H network developed at Φ(Ar) = 1200

fracture surface, representing the cross sectional view of the deposited layer, demonstrated very clearly a columnar growth at the Si:H network initiated by the active presence of Ar with extremely high density in the (SiH_4 + Ar)-plasma in rf glow discharge.

3.6 Raman backscattering studies :

The degree of crystallinity was estimated from the Raman backscattering spectra of the films. Figure 9 shows the Raman spectra in the range 400–600 cm^{-1}, of the films prepared at various Ar dilution. At Φ(Ar) = 60, the microcrystalline nature of the film was identified by the narrow band at 520 cm^{-1} corresponding to the TO vibrational mode of crystalline silicon. Following the method described elsewhere [13], the crystalline volume fraction (X_C) was estimated to be 70%. The crystalline volume fraction increased to 72% when Φ(Ar) was increased to 200, at which the highest electrical conductivity was attained. However, a continuous deviation towards amorphous Si:H network was observed at higher Ar dilution. A broad TO vibrational band of a-Si centered at ~480 cm^{-1} appeared in significant volume, along with the crystalline component at ~520 cm^{-1}, at Φ(Ar) = 400. The full width at half maximum (FWHM) of the crystalline component gradually increased and the overall peak position shifted towards lower wave numbers with the increase in Φ(Ar). However, for Φ(Ar) ≥ 800, an almost amorphous nature of the material was evident by the presence of sole amorphous component at ~ 480 cm^{-1} and no trace of crystalline contribution was identified.

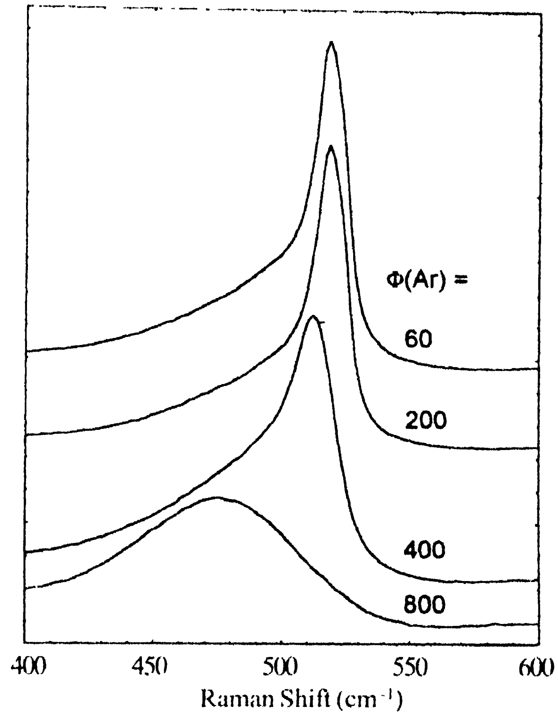


Figure 9. Raman backscattering spectra of Si:H films prepared at various Φ(Ar).

4. Discussion

The Si:H film prepared at a low temperature and low level of electrical excitation to the plasma are normally amorphous in nature when prepared from undiluted SiH_4 or SiH_4 diluted by H_2. Present results demonstrate that Ar dilution to the SiH_4 plasma promotes microcrystallization to the Si:H network. Si : H film prepared at Φ(Ar) = 200 exhibited a σ_D ~ 10^{-5} S cm^{-1} with its very low activation energy ΔE ~ 484 meV. Low optical absorption and small amount of bonded hydrogen incorporated into the network support the microcrystalline nature of the matrix. In addition, the evolution of intense Raman peak around 520 cm^{-1} and sharp crystallographic rings observable in the electron diffraction pattern conclusively signify the microcrystalline nature of the network developed at an Ar dilution of Φ(Ar) = 200. However, the electron micrograph reveals that the μc-Si grains are very much surrounded by amorphous connecting tissues which is the typical feature of the Si:H network when prepared from Ar diluted SiH_4 plasma. This tissue region contributes to the dominating volume fraction of the network, which is made of