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Electrical and optical properties of μc-SiH films

G C DUBEY, R A SINGH, S N MUKHERJEE, SURENDRA PAL and M G RAO

Solid State Physics Laboratory, Lucknow Road, Delhi 110007, India

Abstract. Microcrystalline silicon films have been found quite useful in amorphous silicon solar cells as a contact material in n-i-p cells. Microcrystalline silicon films are obtained when amorphous silicon films are prepared by R.F. glow discharge of $SiH_4 + H_2$ at higher power ratings. These films possess higher conductivity as well as high transmission than amorphous silicon films. The present paper reports the preparation technique of μc-SiH films using R.F. capacitive glow discharge of hydrogen-diluted silane. X-ray studies and TEM studies of the films indicate microcrystallinity of the films. The electrical and optical properties are also reported.

Keywords. Amorphous silicon; solar cells; plasma deposition; thin films

1. Introduction

During recent years several approaches have been adopted for increasing the efficiency of a-SiH solar cells. These include attempts to obtain new configurations of the cell structure and various materials. Use of microcrystalline silicon films for front window material for n-i-p solar cells is one such attempt in this direction. These films have also been used for other thin film devices like thin film transistors. The advantage of microcrystalline film in amorphous silicon solar cell is two-fold; it enhances the transmittance and increases the conductivity of the front layer, thus contributing to an increase in the efficiency of the solar cells. In fact cells upto efficiency of 9·1 % have been reported using μc-SiH films as a front window material in n-i-p cells (Hamakawa and Okamoto 1983).

Veprek and Marecek (1968) were the first to report μ-crystalline films of silicon via chemical transport of silicon in hydrogen plasma. Their aim was to investigate the film growth of μc-silicon at low temperature. Recently, various groups have reported μc-SiH films using glow discharge (Uchida *et al* 1982) or reactive sputtering technique (Hiraki *et al* 1981). There are several methods of producing μc-SiH films i.e. transportation of Si in hydrogen plasma, reactive sputtering technique, increased R.F. power in glow discharge system (Uchida *et al* 1981; Dubey *et al* 1983) and higher substrate temperature. In the present paper μc-SiH films having increased R.F. power as well as higher concentration of hydrogen in silane gas (i.e. 99 % H_2 + 1 % SiH_4) have been grown. At higher concentration of hydrogen the deposition rate also decreases (Vamier *et al* 1984) helping in increasing the crystallite size in the film (Kamuro *et al* 1984). The films have been analyzed by x-ray diffraction and TEM for their microcrystallinity. The electrical and optical properties of these films have been studied and discussed.

2. Experimental

The μc-SiH films were deposited in a capacitively coupled R.F. glow discharge of 1% SiH_4 + 99% H_2. The glow discharge system designed incorporates a stainless steel cross-type chamber as shown in figure 1. This has a parallel plate type of capacitor of 14 cm dia. The distance of the plates can be varied from 1 to 3 inch with provisions incorporated in the top electrode. The bottom electrode on which substrates are kept can be heated through a resistance heater located outside the chamber, up to a temperature of 350°C. The temperature is monitored with a thermocouple provided beneath the bottom electrode of the capacitor and outside the discharge chamber to avoid any contamination. The stainless steel chamber is cooled from outside by circulating cold water through copper tubing cold welded with thermally conductive epoxy. Matsuda (1983) pointed out that higher concentration of hydrogen ions in the plasma tends to yield microcrystalline-hydrogenated silicon films. In the present system, therefore, a higher concentration of hydrogen (99% H_2 + 1% SiH_4) has been used to prepare μc-SiH films by increasing the R.F. power and the concentration of hydrogen in the mixture.

The system is evacuated to 10^{-6} mm of Hg using a diffusion pump. Fomblin oil (HVAC18/8), which is more resistant to reactive gases like silane etc has been used in the diffusion pump. The plumbing line connecting various gaseous systems to the glow discharge chamber is evacuated by a second rotary pump before silane gas mixture (1% SiH_4 + 99% H_2) is admitted into the glow discharge chamber to avoid any contamination of the silane gas mixture. The whole system is also flushed with hydrogen before starting the gas flow. The pressure in the glow discharge chamber measured by Pirani gauge is kept constant by balancing the constant flow of the gas as monitored by rotameter. The compound gauge has been provided close to the rotameter to monitor the pressure in the plumbing line prior to the gas flow. During the gas flow, the constant pressure as indicated in the compound gauge helps in maintaining precise flow control.

The films have been grown on a variety of substrates such as 7059 corning glass, quartz, rocksalt, silicon, cover slips and stainless steel. To study the pattern of delineation for device fabrication, the films have been deposited on the substrate through metal masks. The thickness of the films grown ranges from 300 Å to 1·6 μm. Films with lower thicknesses were used for TEM studies.

R.F. power is fed through a coaxial cable having n-connector and fed to the parallel plate capacitor through power meter (model 4410). Both the transmitted and the reflected power is measured from which the actual power fed to the system is computed. No provision was made to scavenge the exhaust silane gas by burning as is normally the practice, since highly diluted silane is used in the experiment.

The substrate temperature has been varied from room temperature to 200°C. Different gas flow rates have also been tried. Most of the work have been done at slow deposition rates and at substrate temperature of 200°C where good quality films are obtained.

X-ray diffraction studies have been carried out on Philips x-ray diffractometer and optical absorption measurements on spectrophotometer (Cary 17) TEM has been done on electron microscope (JEOL). For thickness measurements Taly surf and light sectioning microscope have been used.

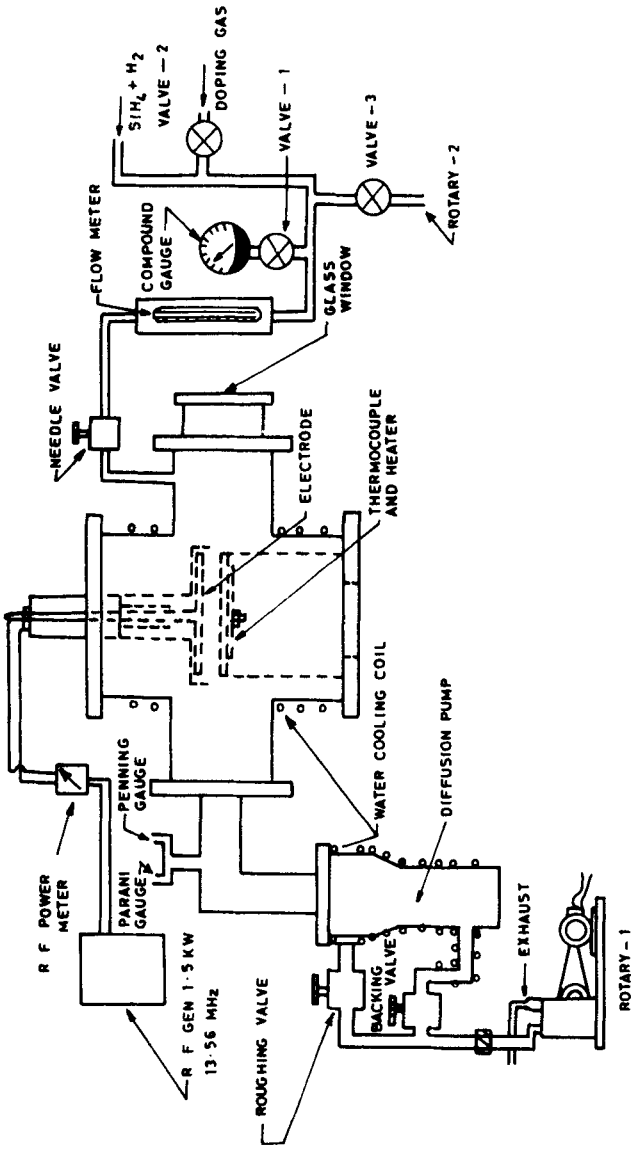

Figure 1. Schematic of glow discharge system.

3. Results and discussion

The films obtained were smooth having very good adhesion and difficult to scratch except those which were deposited at room temperature. All the films withstood the tape test as applied to thin films. The pattern delineation showed sharp edges. X-ray diffraction pattern provides information on the crystallite size, its orientation, lattice distortion and the volume fraction of crystalline phase in mixed phase of μc-SiH. Figure 2 shows the x-diffraction pattern of 1 μ thick film deposited on silicon substrate. Similar measurements were carried out by Uchida *et al* (1981) indicating the diffraction line of (111) phase characteristic of silicon. The diffraction pattern of the film taken on glass substrate indicated peaks at $2\theta = 28{\cdot}8°$, 48° and 56°, showing that the film contains mixed phase of perfect crystalline phases of (111), (220), (311) and others along with amorphous phase.

In order to estimate the degree of crystallinity of the film, the substrate was heated to 700°C for 1·5 hr in hydrogen atmosphere. This temperature is quite above the transition temperature of 650°C for crystallization of the entire film. Normally, the complete film is not crystalline. Percent volume fraction of crystalline phase varied from 60 to 80%. Previous studies had reported this value from 20 to 80% depending upon the R.F. power (Nakatani *et al* 1983). Figure 2 enables one to calculate the percentage volume fraction of microcrystals. It is seen that the values of peak heights I_p and the full width at half maximum (FWHM) $\Delta 2\theta$ are different before and after annealing. Assuming that the product of I_p and (2θ) is proportional to the volume of microcrystals in μc-SiH film, the volume fraction in the film has been estimated as 70%. It has been observed that $\Delta 2\theta$ which is a measure of the micro-crystallite size remains constant upto the annealing temperature of $\simeq$ 500°C. On annealing at 700°C, a two-fold increase in the crystallite size is observed. The crystallite size in the as-grown film is calculated to be 150 Å using the Scherrer formula (Cullity 1959).

Figure 3 shows the electron diffraction pattern of the three types of films deposited at

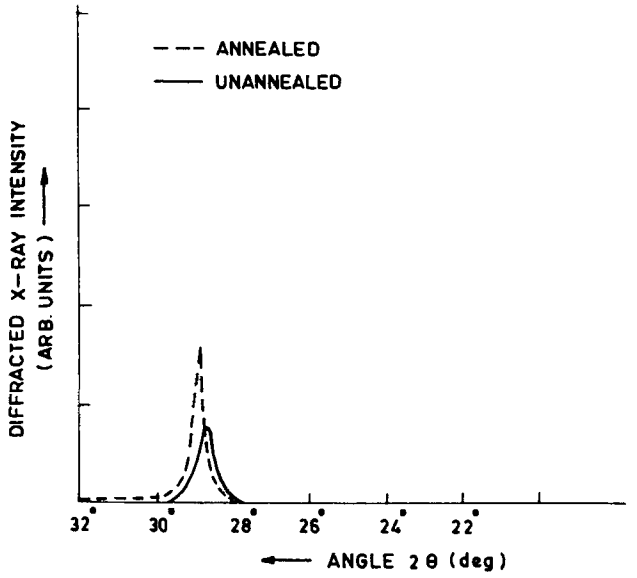

Figure 2. X-ray diffraction pattern.

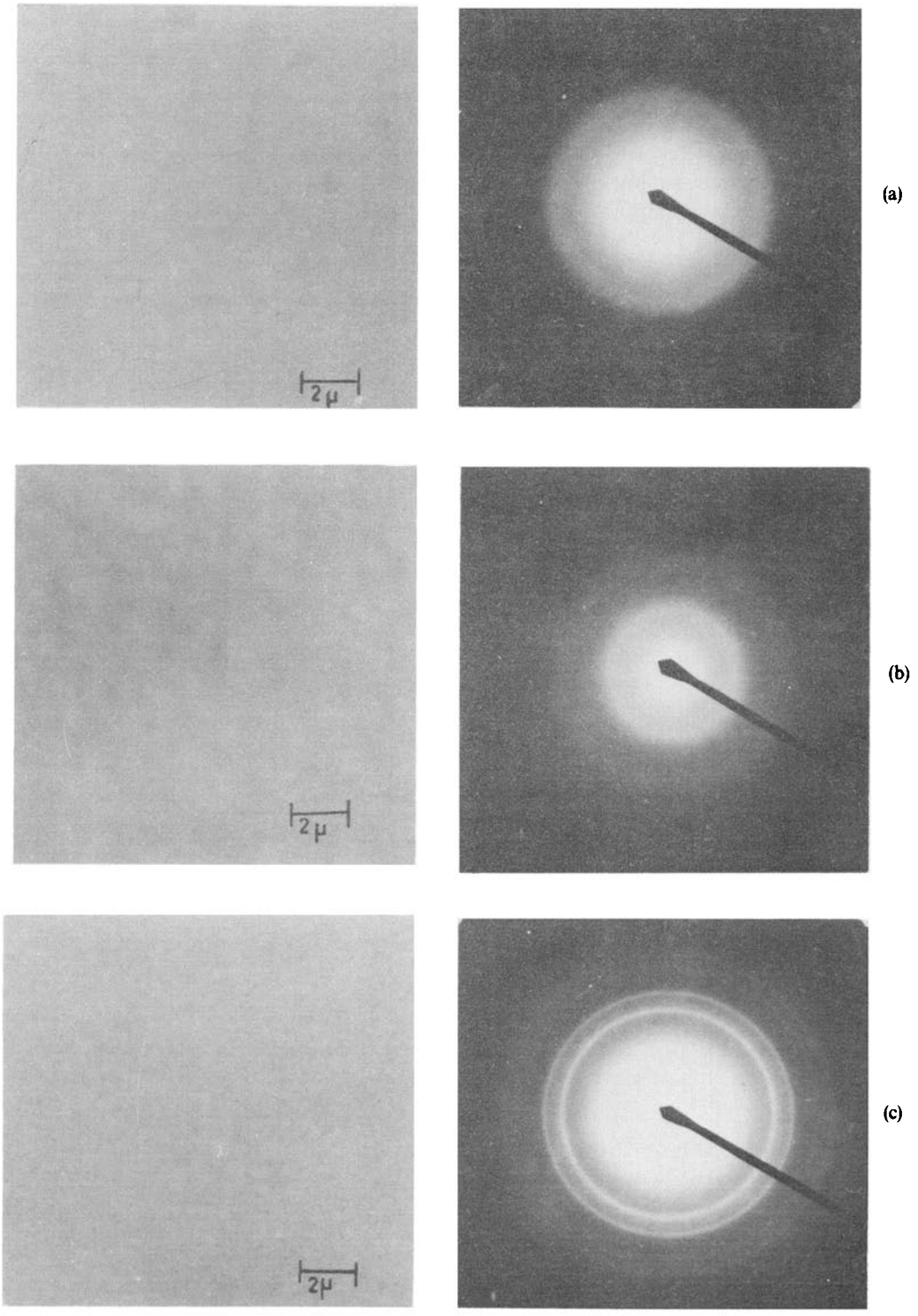

Figure 3. Photomicrograph of amorphous and microcrystalline films along with SAD. The microcrystallinity increases as the power increases (**a**) 20 watt, (**b**) 50 watt (**c**) 150 watt.

power level of 20, 50 and 150 watts. The Debye Scherrer rings of the diffracted pattern show a gradual increase in microcrystallinity with increase in power. Also, even at smaller thicknesses in the range of 400–500 Å the films are microcrystalline.

The optical bandgap E_0 of μc-SiH film has been calculated using figure 4, where α^2 has been plotted against photon energy, since the μc-SiH films are used for front window material. In the figure, α^2 has been plotted to compare the results with those of other transparent conducting materials like tin oxide films (Dubey *et al* 1985).

The bandgap obtained is $\simeq$ 1·8 eV which conforms to the data obtained by Uchida *et al* (1981). Figure 5 shows the plots of $h\nu$ vs $\sqrt{\alpha h\nu}$ for μc-SiH, a-SiH and silicon. The data of a-SiH(a) and silicon (c) have been taken from Tanaka and Matsuda (1983). It is seen that the spectra of μc-SiH and single crystal silicon do not obey the square root law and that a-SiH exhibits a linear variation of $\sqrt{\alpha h\nu}$ over a wide $h\nu$ range.

A comparison of the curves shows that the nature of μc-SiH lies between a-SiH and C-Si. This indicates that with increased power, it is possible to get crystalline films and the optical properties are therefore changed accordingly. This also is indicative of the

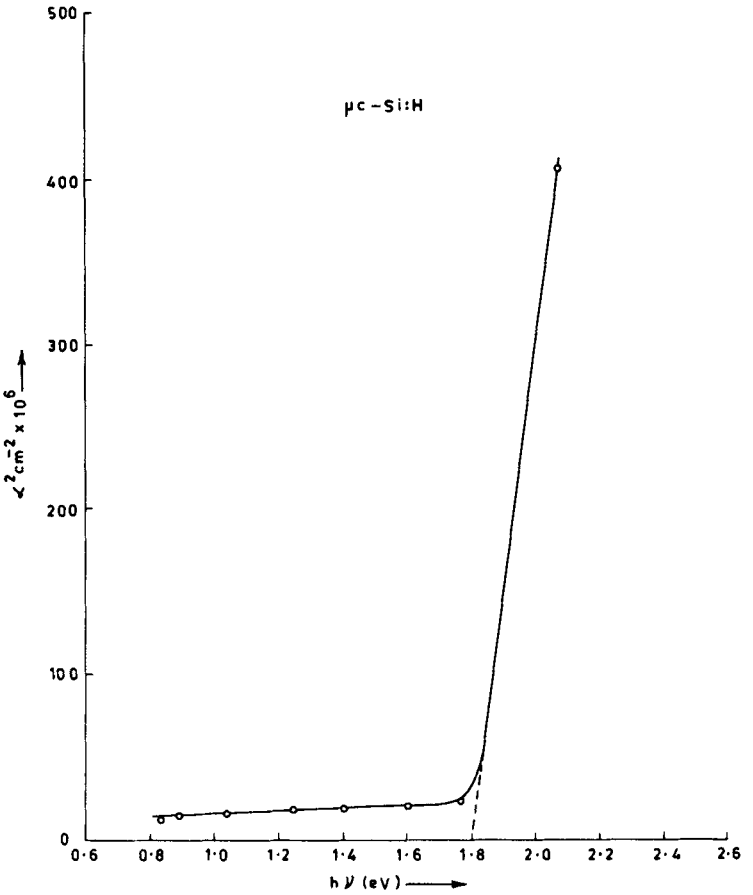

Figure 4. Variation of α^2 with photon energy.

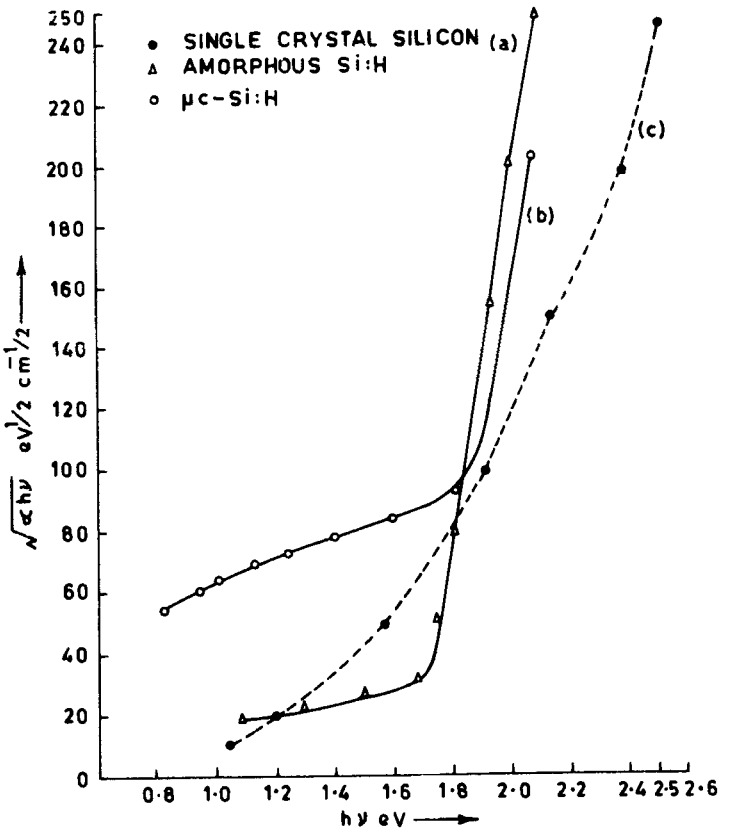

Figure 5. Variation of $\sqrt{\alpha h\nu}$ with photon energy.

fact that these films have a mixed phase of amorphous and crystalline substances of smaller crystallites.

As mentioned earlier these microcrystalline films have been used as window material in n-i-p solar cells. Therefore, the transmission data of these films is very useful. Figure 6 shows the transmission with varying thickness for λ = 7,000 Å. It has been suggested that a thickness of around 100 Å to 200 Å is required in the fabrication of n-i-p solar cells (Tanaka and Matsuda 1983).

4. Electrical properties

Dark conductivity σ_d of μc-SiH is in general two or three orders of magnitude higher than a-SiH (Tanaka and Matsuda 1983; Kaya *et al* 1984). Similar results have been observed in the present study. Moreover as shown in figure 7, the resistivity of the film is a function of substrate temperature. It is also seen that as substrate temperature is increased the resistivity decreases which can be attributed to increase in crystallite size with increase in substrate temperature. The variation of electrical resistance of the film with temperature is given in figure 8.

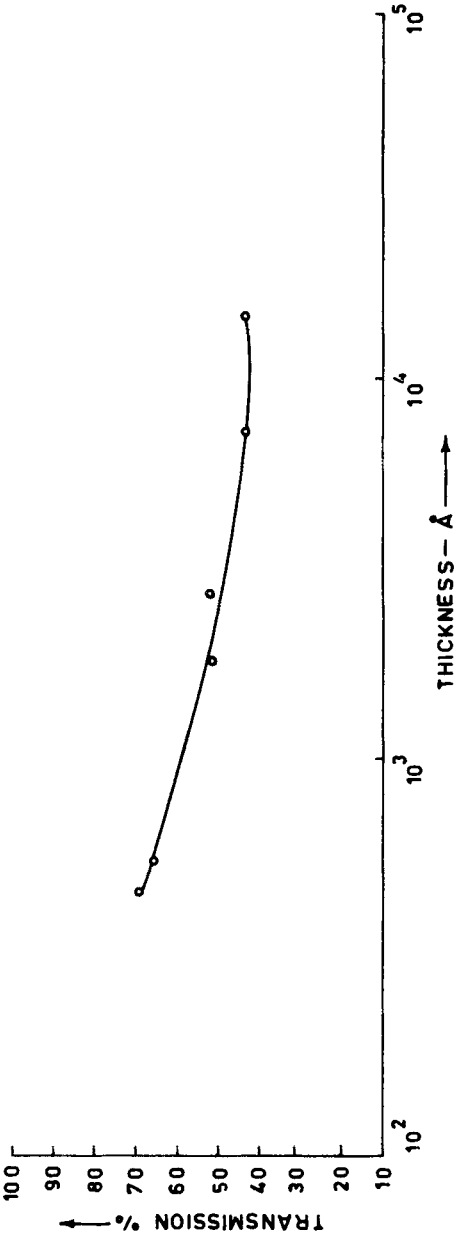

Figure 6. Variation of transmission with thickness of μ-crystalline films.

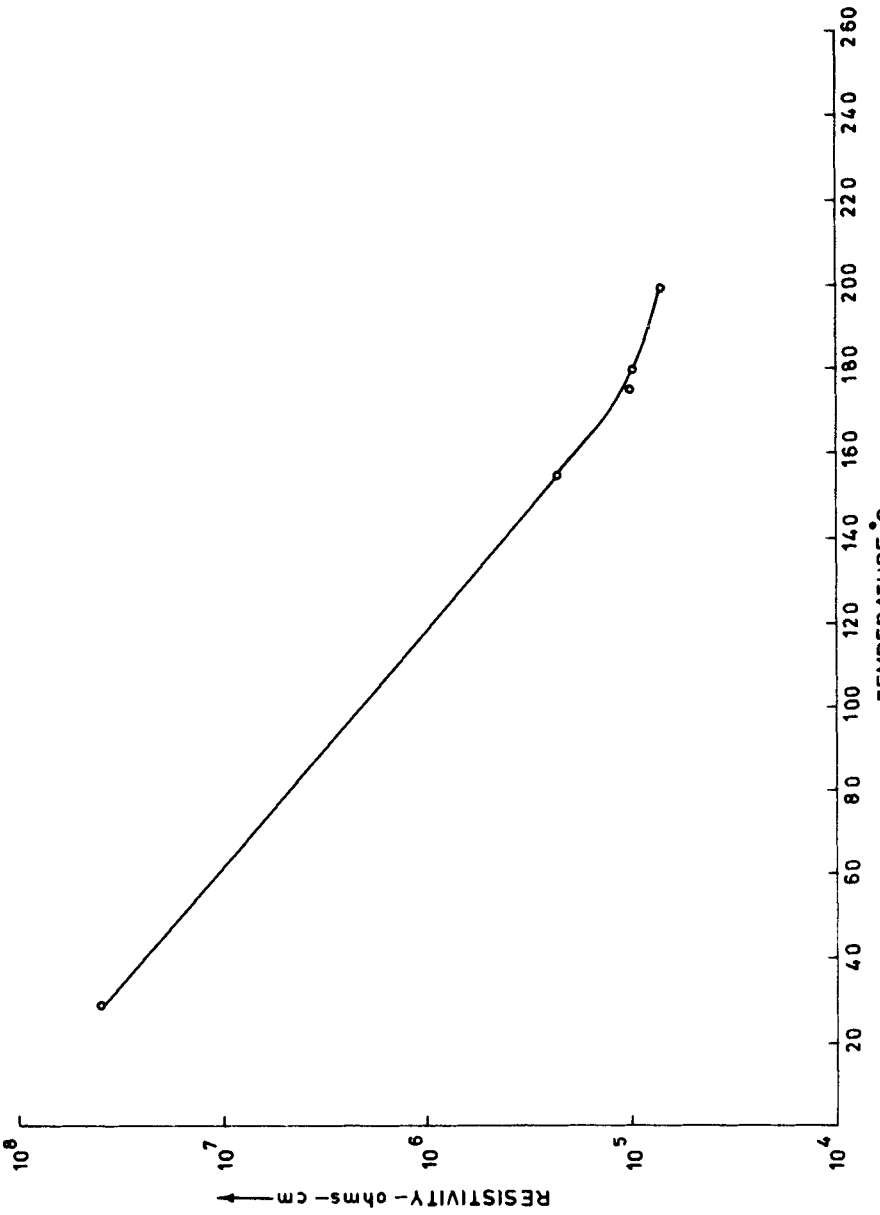

Figure 7. Variation of resistivity with deposition temperature.

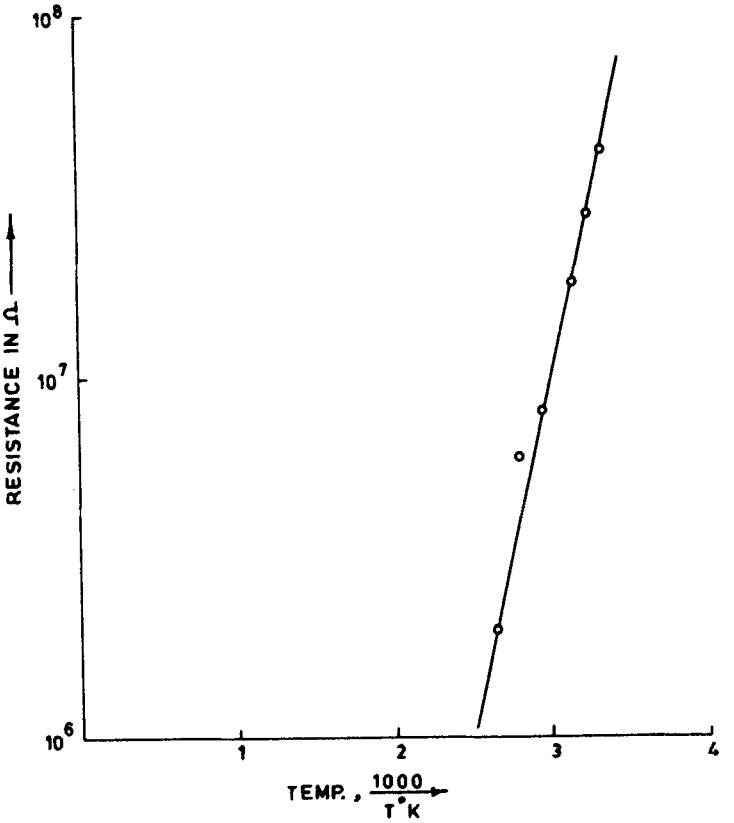

Figure 8. Variation of electrical resistivity with temperature for films grown at 200°C.

5. Conclusions

μc-SiH films are produced when hydrogen diluted silane is decomposed in a parallel plate capacitive glow discharge system with power level of 50 watt and above. Structurally, these films are of mixed phase of amorphous and crystalline silicon as confirmed by annealing the films upto 700°C in hydrogen atmosphere. The resistivity of the films decreases as the substrate temperature is increased.

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References

Cullity B D 1959 *Elements of x-ray diffraction* (Massachusetts: Addison-Wesley) 99

Dubey G C, Singh R A, Pal S and Gopal Rao M 1983 Second International Workshop on the Physics of Semiconductor Devices, New Delhi

Dubey G C, Singh R A, Pal S and Gopal Rao M 1985 *Photovoltaic materials and devices, Proc. Symp.* (eds) B K Das and S N Singh (Delhi: Wiley Eastern) p. 254
Hamakawa Y and Okamoto H 1983 *Amorphous Semiconductor Tech. Devices* **6** 182
Hiraki A, Imura T, Modi K and Tashiro M 1981 *J. Phys. (Paris)*, **C-4** 277
Kaya H, Imura T, Kusao T, Hiraki A, Nakamura O, Okayasu Y and Matsumura M 1984 *Jpn. J. Appl. Phys.* **23** L549
Kamuro S, Aoyagi J, Segawa Y, Namba S, Masuyama A, Matsuda A and Tanaka K 1984 *J. Appl. Phys.* **56** 1658
Matsuda A 1983 *J. Non-Cryst. Solids* **59–60** 767
Nakatani K, Yano M, Suzuki and Okinawa A 1983 *J. Non-Cryst. Solids* **59–60** 827
Tanaka K and Matsuda A 1983 *Amorphous Semiconductor Tech. Devices* **6** 161
Uchida Y, Ichimura T, Veno M and Haruki H 1982 *Jpn J. Appl. Phys.* **21** 1586
Uchida Y, Ichimura T, Veno M and Ohsawa M 1981 *J. Phys. (Paris)* **C-4** 265
Vamier P E, Kampas F J, Corderman R R and Rajeswaran G 1984 *J. Appl. Phys.* **56** 1812
Veprek S and Maracek V 1968 *Solid State Electron.* **11** 683