REDUCTION OF $SiCl_4$ IN HYDROGEN R.F. DISCHARGES AT LOW PRESSURES

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ABSTRACT

Preliminary results on amorphous silicon films obtained by reduction of $SiCl_4$ under hydrogen r.f. discharges at pressures between 1-5 torr are presented. X-ray diffraction, IR and ESR spectroscopic techniques, optical absorption, index of refraction and room temperature electrical measurements were used for chemical and physical characterization of the deposited films.

1. INTRODUCTION

The current interest in thin film depositions from reactive plasmas is related to the polymerization of a wide variety of organic and silicon compounds (1) and to the treatment, coupled to dry-etching techniques, of semiconductor surfaces utilized for the manufacturing of integrated electronic circuits (2), and more recently (3), to the preparation of amorphous silicon films. The decomposition of SiH_4 in radiofrequency discharges has been successfull used for the production of hydrogenated a-Si films. When used as photovoltaic converter, a-Si films have electrical and optical properties more suitable than single crystal silicon. The values of the optical band gap, of the visible absorption coefficient and of the efficiency forphotovoltaic energy conversion are close to the optimum for semiconductor homojunctions (4). The films obtained by the glow discharge decomposition of silane have peculiar characteristics: the density of the gap states is sufficiently low and sufficiently well characterized to allow usefull doping.

However, very little about the method starting from $SiCl_4$ (5,6) has been studied in a systematic manner. A systematic investigation of the deposition conditions implyes the knowledge of the effects on the deposited film characteristics of a large number of variable parameters. The gas pressure, temperature and composition, the total gas flow rate and residence time, the reactor geometry, the power input, the substrate material, position and temperature, are all variable which, need to be explored in finding the appropriate operative conditions for high quality film deposition.

2. EXPERIMENTAL

The experimental apparatus is schematically shown in fig.1. It is essentially made by a Pyrex tube (8 cm, i.d.), surrounded by a water jacket and capacitively coupled to a 35 MHz radiofrequency generator by means of two external annular electrodes, which can be set at different distances (7). A fixed separation of 10 cm, including the electrode heights has been used for this study. The substrate for the films were set on a Pyrex "pedestal" positioned 1 cm below the lower electrode and equipped with a resistor for the heating and a thermocouple for temperature measurements. The reactor was feeded with $SiCl_4/H_2$ gaseous mixtures, containing 5-10% of $SiCl_4$ vapor. The required gaseous flow of $SiCl_4$ was obtained by bubbling metered flow of hydrogen through liquid SiCl4 kept at 25 °C constant temperature. The feeding mixture composition was controlled by gaschromatographic analysis.

The unreacted $SiCl_4$ and the discharge products were flowed through a soda-lime trap to prevent them to reach the rotary pumps.

The reactor has been also equipped with thin quartz probes, positioned at different heights into the reactor and connected to an independent pumping system which will be used for the analysis of the discharge products. Total flow rates in the range of 50-200 sccm, power input of the order of 100-200 watts, substrate temperatures between 100 and 500 °C and pressures between 1-5 torr were used. As film substrate we used sapphire, alumina, crystalline Si{111}, fused quartz and corming glass.

3. RESULTS AND DISCUSSION

The films obtained were hard, well adherent to the substrate, and presented variable colours depending on the growth conditions. Their thickness, measured from interference fringes of optical trasmission curves ranged from 0.4 to 1.8 μm, depends on the discharge duration, on the distance of the substrate from the bottom of the discharge and on the substrate temperature. Films grown at constant distance from the discharge zone and constant substrate temperature have shown a linear relationship between thickness and discharge duration at least for the first 50 minutes. Deposition rates ranging from 350 to 500 Å min^{-1} have been determined under these experimental conditions.

X-ray diffraction pattern obtained with a film grown on alumina, at 400 °C and p=2torr, is shown in fig.2. The main feature of this diffraction spectrum is the presence of a broad band, approximately centered at an angle $2\theta = 28.4°$ which corresponds to Bragg reflection from {111} plances of crystalline Si. Such pattern is indicative of an amorphous material (8).

The number of dangling bonds, which give rise to states in the energy gap, have been measured by ESR determination of the spin density. Typical ESR signal for a film deposited on Corning glass at 150 °C is reported in fig.3. The signal, for which a g-factor of 2.0051 has been evaluated, was obtained in an X-band microwave bridge with the sample at room temperature in a 9 in. magnet. The dangling bond density derived by comparison with a known amount of DPPH was found to be 10^{16} cm^{-3}. This value should be compared with the ones reported in literature for conventionally prepared a-Si, which range from 10^{19} - 10^{20} cm^{-3}, and those obtained from glow discharge, which have much fewer dangling bonds, about 10^{18} cm^{-3} for room temperature deposit and 10^{16} cm^{-3} for 250 °C grown films (3). The

refractive index, derived from optical absorption measurements, is reported in fig.4 as function of wavelenght. Results from ref.(6,9) have been also included for comparison. Our data are in good agreement with those of Plättner et al. (6) and those quoted in literature (10). Since the deposition temperature for the majority of our films is higher than that used in ref.(6), lower values of refractive index are expected for our films, in accordance with the literature reported behaviour (10).
The electrical resistivity and the Hall mobility, measured at room temperature using the Van der Pauw's method, have been found to vary between $10^3 \div 10^5 \Omega$cm and 5-20 $cm^2 V^{-1} s^{-1}$, respectively.
More significant data cannot be reported in the present note since systematic measurements have not been yet performed.

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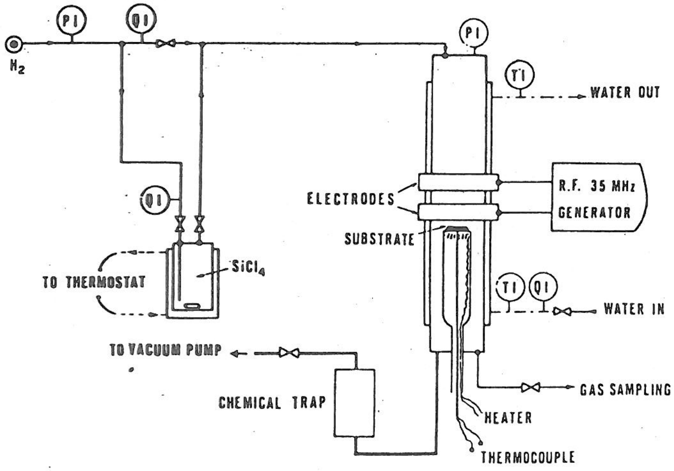

Fig. 1 - Schematic diagram of the apparatus for reactive plasma deposition (RPD).

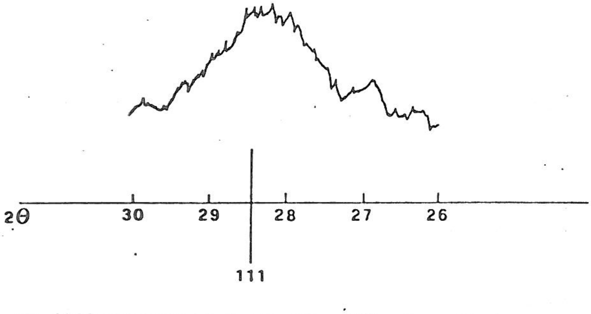

Fig.2 - RX diffrattometric trace of a film deposited on alumina (T_s = 400°C).

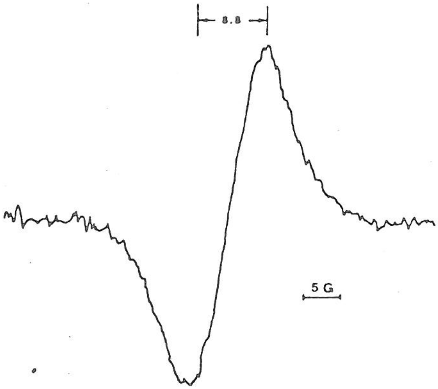

Fig.3 - ESR first derivate spectrum of a film deposited at 150°C.

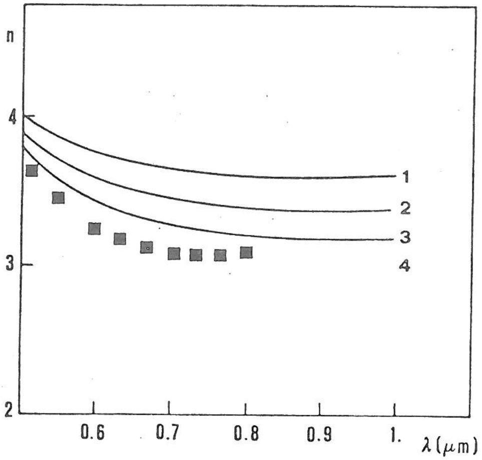

Fig.4 - Room-temperature index of refraction of cristalline silicon (curve 1, (8)); hydrogenated amorphous silicon from SiH_4 (curve 2, (11)); hydrogenated amorphous silicon from $SiCl_4$ (curve 3, (11) and curve 4, present work).