Powder Dissipation in PECVD for $\text{SiH}_4\text{-CH}_4\text{-H}_2$ Gas Mixtures

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ABSTRACT. The effective dissipated power in $\text{SiH}_4\text{-CH}_4\text{-H}_2$ plasmas excited by 13.56 MHz has been measured for different gas ratios using a subtractive technique to take into account the effects of power losses in the rf circuit. It is found that the dissipated power in general increases with increasing CH_4 concentration and decreases with increasing H_2 concentration. Optical, electrical and defective properties of films deposited under a wide range of deposition conditions have been measured and correlated with dissipated power.

1. INTRODUCTION

It is well known that pure SiH_4 can be dissociated in plasma enhanced chemical vapor deposition (PECVD) systems excited by rf at 13.56 MHz at relatively low power densities (about $1\text{-}2 \times 10^{-2} \text{ W/cm}^3$). In these conditions high quality a-Si:H films having very good electrical properties can be deposited [1]. Amorphous silicon-carbon alloys (a-SiC:H) are also normally deposited using the PECVD method. This generally employs gas mixtures of silane (SiH_4), methane (CH_4) and hydrogen (H_2) in a capacitively coupled system using 13.56 MHz plasma excitation [2]. Variations in the ratio of the gases in the mixture allow film composition and characteristics to be controlled within a wide range. Other parameters such as total flow, pressure, deposition temperature and rf power also have a remarkable effect on film characteristics. These parameters usually can be controlled by setting the values on the instrumentation of the PECVD system; the set value is then kept constant by some feedback loop. The capability of a deposition system to keep constant the deposition parameters is fundamental in allowing films with the same optoelectronic properties to be reproduced from run to run. However, experimental parameters are not truly independent each other, and a variation of one of them can make another parameter change as well. In particular the effective power dissipated in the plasma depends on a number of plasma parameters other than the power delivered by the rf generator, such as the impedance of the discharge and the impedance of the rf delivery circuit, including the matching network. The impedance of the discharge changes according to various process parameters, such as gas flow and mixture, pressure, pumping speed and generator power which determine the composition of the plasma (molecules, ions and free radicals) and the dwell time of the species. It follows that as some process parameters change at constant generator power the effective power dissipated in the plasma changes.

In this paper we report on measurements of the effective power dissipated in $\text{SiH}_4\text{-CH}_4\text{-H}_2$ plasmas of a 13.56 MHz PECVD system with varying methane and hydrogen fraction by using a subtractive technique [3,4]. The deposition rate, the optical, electrical and defective properties have been determined and correlated to the plasma conditions. The effective dissipated power P_d is strongly influenced by gas mixture composition: it increases with increasing methane fraction and decreases with increasing hydrogen fraction. Deposition rate and energy gap increase as a function of P_d and the degradation of electrical and defective properties are directly correlated to energy gap.

2. EXPERIMENTAL

A new modular UHV multichamber PECVD system based on the cluster concept was used for depositing the amorphous silicon-carbon thin films [5]. The system was designed by MVSystems Inc., Golden, Colorado, and constructed jointly with Elettroviva S.p.A., Torino, Italy. The system contains four modular UHV PECVD chambers of stainless steel construction (Modular Process Zones or MPZ's) located around a central chamber which contains the transport system (Isolation and Transfer Zone or ITZ) and serves the function of a load lock to allow introduction of the substrates (10 cm x 10 cm) into the MPZ's. The MPZ's are separately pumped using turbomolecular pumps via throttle valves and have separate gas manifolds; pumping of the process gas takes place via the turbomolecular pumps and the throttle valves. Each MPZ is complete with electrodes (anode and cathode), the distance between which can be internally altered between 1 and 5 cm. Each MPZ is complete with its own gas manifold with three to five mass flow controllers and associated control unit. A radio frequency generator (13.56 MHz) and an automatic matching network are switchable between the different MPZ's to enable the PECVD process to take place.

The a-SiC:H films have been deposited in $\text{SiH}_4 + \text{CH}_4 + \text{H}_2$ gas mixtures with methane fraction $Y(\text{CH}_4) = \phi(\text{CH}_4)/(\phi(\text{CH}_4) + \phi(\text{SiH}_4))$ in the range 0-0.97 and hydrogen dilution $Y(\text{H}_2) = \phi(\text{H}_2)/(\phi(\text{CH}_4) + \phi(\text{SiH}_4) + \phi(\text{H}_2))$ in the range 0-0.99, where ϕ indicates the flow of the respective gas. The power supplied by rf generator P_n was varied between 4-8 W. The other deposition parameters were kept constant: deposition pressure 100-130 Pa, substrate temperature 180 °C, electrode distance 14 mm, substrate area 100 cm².

A method to determine the effective power dissipated in the discharge is described in ref [3]. This technique takes into account the power loss in the rf circuit, and requires that for a particular system the power delivered by the generator with no plasma is measured as a function of the electrode voltage, and then this curve is subtracted from the curve of power measured with plasma on. Since in a real system the power-voltage curve (and therefore the power loss) may vary with some minor changes in cabling position or mechanical setup, it is advisable to repeat the measurement prior to each deposition, which makes this technique quite lengthy.

The method used in this paper, which is described in ref. [4], simply requires the measurement of the power and the voltage with no plasma (P_0 , V_0) and with plasma (P_i , V_i), both after having tuning the matcher to resonance. The circuit used to measure the effective power is shown in Fig. 1a. Based on the assumption that a matching network is a linear system, the P - V^2 curve is a straight line with slope $G_0/2$ (see Fig. 1b), where G_0 is the equivalent matcher conductance in resonance condition. When the plasma is initiated and the matcher is tuned again to resonance, the system shifts to a straight line with slope $(G_0 + G_d)/2$, in which G_d is the plasma conductance. The corresponding voltage at the electrode is now V_i , and the real power dissipated P_d is given by

$$P_d = P_i - P_0 \left(\frac{V_i}{V_0} \right)^2$$

We have measured the effective power dissipated in mixtures of SiH_4 with CH_4 and H_2 for different flows of these gases, so as to obtain plasmas with different composition, gas dissociation and residence time. The power delivered by the generator is measured by a power meter at the output of the generator; the rf voltage on the electrode is measured by an rf probe on the rf line between the matching network and the electrode.

The effects of the power dissipated in the plasma on a-Si:H and a-SiC:H films have been monitored through deposition rates, optical, electrical and defective properties. Deposition rates have been evaluated from film thickness and deposition time. Absorption coefficients for photon energies above the optical gap have been obtained by transmittance-reflectance spectroscopy following a procedure reported in ref. [6]. Due to the difficulties to use the Tauc's gap [7] in a-SiC:H materials, the E_{04} optical gap, defined as the energy at which $\alpha = 10^4 \text{ cm}^{-1}$, was used. Dark and photo conductivities have been measured under vacuum (10^{-2} Pa) in coplanar configuration by means of a Keithley electrometer with internal source. The photoconductivity was measured under a 100 mW/cm²

AM2.0 lamp. The defect densities have been obtained by electron spin resonance technique by using a Bruker-ESR instrument. The spin density has been determined by comparison with standard samples.

Fig. 1a - Equivalent circuit of a PECVD system

Fig. 1b - Typical P - V^2 plot

3. RESULTS AND DISCUSSION

Fig. 2 reports the effective power dissipated (P_d) in a SiH_4 - CH_4 plasma ($\text{H}_2=0$) for $Y(\text{CH}_4)$ fractions varying between 0 and 1 at different powers supplied by the rf generator (P_n). It can be seen that the effective power dissipated slightly increases with CH_4 fraction. This can be explained considering the ionization reactions of CH_4 molecules, at energies below the SiH_4 dissociation threshold [8]. Fig. 3 reports the effective power dissipated in a SiH_4 - CH_4 - H_2 plasma for three different CH_4 fractions (0, 0.4 and 0.72) and $Y(\text{H}_2)$ dilution varying between 0 and 0.99. It is evident that the effective power dissipated strongly decreases with increasing H_2 flow rates. This can be due to the higher ionization and dissociation energy of H_2 with respect to the ionization energy and the dissociation energy respectively of CH_4 and SiH_4 molecules [9].

Fig.2 - Effective power P_d dissipated in a PECVD plasma of SiH_4+CH_4 as a function of $Y(\text{CH}_4)$ for different power P_n supplied by the rf generator.

Fig. 3 - Effective power P_d dissipated in a PECVD plasma of $\text{SiH}_4+\text{CH}_4+\text{H}_2$ as a function of $Y(\text{H}_2)$ for different $Y(\text{CH}_4)$ fractions at a constant power delivered by rf generator, $P_n=4\text{W}$.

The deposition rates d_r are markedly influenced by the effective dissipated power P_d in the plasma. Fig. 4a shows d_r as a function of P_d for some of the a-SiC:H films of Fig. 2, deposited with different CH_4 fraction and at different power supplied by the rf generator. For all gas mixtures the effect of an increase of P_d is reflected in an increase in d_r , as expected by a higher dissociation of SiH_4 molecules as the dissipated power density increases. Since the deposition rate as a function of $Y(\text{CH}_4)$ for pure SiH_4+CH_4 gas mixtures at a constant power supplied by rf generator P_n vanishes for pure methane plasma (Fig. 4b), we can deduce that the discharge operates in the so called "low power regime" [10, 11]. The methane decomposition threshold is not reached and only the SiH_4 molecules are decomposed. The incorporation of carbon takes place through chemical reactions between CH_4 and the SiH_n reactive species.

Fig. 5 shows the trend of the deposition rates as a function of the effective dissipated power P_d in the plasma for films deposited at different H_2 dilution in pure SiH_4 and for $Y(\text{CH}_4)=0.4$. An increase

of the deposition rate, as P_d increases, can be observed and we want to stress that the variations of P_d are a consequence of H_2 dilution (see Fig. 3). It is known that when in a $SiH_4+CH_4+H_2$ plasma hydrogen dilution exceeds 99% microcrystal formation occurs and the deposition rate drops to values below 0.05 nm/s [12, 13]. This decrease of deposition rate is usually attributed to surface etching due to atomic hydrogen. The results reported in Figs. 3 and 5 suggest that also the decrease of P_d when hydrogen dilution is applied to SiH_4+CH_4 gas mixtures has to be taken into account to explain the decrease of d_r .

Fig. 4a - Deposition rate d_r of a-SiC:H films as a function of the power dissipated in SiH_4+CH_4 plasma for different $Y(CH_4)$ fractions.

Fig. 4b - Deposition rate d_r of a-SiC:H films as a function of $Y(CH_4)$ fractions for a constant power of 4 W supplied by the rf generator.

Fig. 5 - Deposition rates d_r as a function of power dissipated in the plasma for a-Si:H and a-SiC:H films deposited by PECVD in different H_2 diluted gas mixtures, at a power supplied by rf generator $P_n = 4$ W.

Fig. 6 reports the E_{04} optical gap as a function of the power dissipated in the SiH_4+CH_4 plasma at different $Y(CH_4)$ fractions. It is possible to see that the energy gap is slightly enlarged by increasing P_d , more markedly for high CH_4 fraction. A possible explanation can be found in a different carbon and hydrogen incorporation induced by the different dissipated power in the plasma

Fig. 6 - Energy gap E_{04} as a function of dissipated power in the SiH_4+CH_4 plasma for different $Y(CH_4)$ fractions.

Fig. 7 shows the dark and photoelectrical conductivity as a function of E_{04} optical gap for the a-SiC:H films of Fig. 6 and for device-quality a-SiC:H films taken from refs. [14, 15]. We can observe the same trend of photoconductivity as a function of energy gap, independently from the dissipated power in the plasma. Therefore it is apparent that in the range of dissipated power we have investigated (1.8-4.8 W) the main effects are an increase of deposition rate and a change of carbon/hydrogen incorporation, which reflects in an increase of the energy gap. This indicates that the increase in power increases the dissociation rate of the molecules but does not have a relevant effect on the dissociation mechanism, which are still those typical of the "low power regime". The density of spins N_s as a function of energy gap, is reported in Fig. 8 for the same samples of Fig. 7. There are no remarkable differences in defect density for samples with the same energy gap deposited by different dissipated power. N_s increases, as energy gap enlarges, from about 10^{16} - 10^{17} cm^{-3} for E_{04} of 2.0-2.1 eV until it saturates at values of 10^{18} cm^{-3} for E_{04} above 2.25 eV.

Fig. 7 - Dark and photoelectrical conductivity as a function of E_{04} energy gap for the same a-SiC:H samples of Fig. 6.

Fig. 8 - Density of spins N_s as a function of E_{04} energy gap for the same a-SiC:H films of Fig. 6.

4. CONCLUSIONS

In summary, through a subtractive technique, the effective dissipated power in SiH_4 - CH_4 - H_2 plasmas obtained by 13.56 MHz PECVD has been measured for different gas fluxes. It has been shown that in SiH_4 + CH_4 gas mixture, as $Y(CH_4)$ increases the dissipated power increases, while it decreases as H_2 dilution increases. The main influence of the power on the deposited a-SiC:H films is on the deposition rate and the energy gap, probably due to a different incorporation of carbon and hydrogen. The optoelectronic properties and the defect densities show, independently from the dissipated power in the range 1.8 - 4.8 W, the same trend as a function of energy gap as for device quality a-SiC:H. Further investigation on structural and compositional properties are in progress.

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