DEPOSITION OF SEMICONDUCTING AND DIELECTRIC FILMS IN "DUAL-" AND "SINGLE-MODE" MICROWAVE OR RADIO FREQUENCY PLASMAS

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ABSTRACT

Thin films of hydrogenated amorphous silicon, silicon oxide and organosilicon have been deposited in microwave (MW, 2.45 GHz) and radio-frequency (RF, 13.56 MHz) glow discharges, performed simultaneously or separately. The RF - induced negative DC self-bias voltage applied to the substrates is shown to strongly affect plasma-chemical reactions, causing significant changes in the deposition rate, film composition and electrical properties.

1. INTRODUCTION

Thin film deposition in microwave (MW) discharges generally leads to substantially higher deposition rates than in lower frequency discharges /1/. This is the consequence of higher concentrations of growth precursors in the gas phase, due to differences in the electron energy distribution functions /2/. On the other hand, interactions of charged species with surfaces exposed to the plasma are more pronounced at lower excitation frequencies /3/. The commonly used capacitively coupled radio-frequency (RF) discharge is characterized by a plasma sheath region near the RF powered electrode, leading to a pronounced negative DC self-bias voltage /3/. It follows that the biased electrode is subjected to bombardment by positive ions. This effect is exploited in plasma processes such as sputtering, reactive ion etching, deposition of "diamond-like" carbon films, composite films containing metal clusters and their modification /4/. Therefore, important effects on the film structure and properties when both MW and RF power are applied simultaneously can be expected. We concentrate in this report on the deposition, structure, and properties of hydrogenated amorphous silicon (a-Si:H), plasma silicon oxide (P-SiO_x), and plasma polymerized hexamethyldisiloxane (PP-HMDSO). We compare the results with the characteristics of similar films obtained from pure MW plasma in our earlier studies /5-8/.

2. EXPERIMENTAL DETAILS

The depositions were carried out in a large volume microwave plasma (LMP) apparatus /7/. The MW power (2.45 GHz) was applied from a periodic slow wave structure through a fused silica window facing a substrate holder, a 13 cm diameter aluminum electrode capacitively coupled to a 13.56 MHz power supply. The negative DC self-bias voltage V_s developed at the substrate holder was measured with a voltmeter, using an RF choke. For the range of bias values studied here ($-400 < V_s < 0$ V), the corresponding RF power ranged from 200 W to 0 W, respectively. The applied MW power was kept constant at 150 W throughout.

The a-Si:H films were deposited at 100 mTorr from SiH_4 at a flow rate of 8 sccm, or from a mixture (SiH_4/Ar ~ 8 sccm/42 sccm). P-SiO_x films were prepared at a total pressure of 80 mTorr from a SiH_4/N_2O ~ 10 sccm/30 sccm feed gas mixture; PP-HMDSO films were grown at 50 mTorr using a 10 sccm flow of the HMDSO monomer. P-SiO_x and PP-HMDSO were deposited at ambient substrate temperature (T_s = 25°C), whereas a-Si:H was prepared at T_s = 250°C.

The film thicknesses on silicon wafers were measured using a Leitz MPVSP multiple wavelength optical interferometer. Film compositions were determined by X-ray photoelectron spectroscopy (XPS) in a VG ESCALAB 3 MK II system. In some cases the hydrogen concentration in the films was measured by nuclear elastic recoil detection analysis (ERDA). Dielectric losses (tanδ) of the insulating films, deposited onto glass substrates with preevaporated Aℓ electrodes, were measured at room temperature in vacuum using a Hewlett Packard 4274A LCR meter. The light-to-dark conductivity ratio R ($\equiv \sigma_{ph}/\sigma_d$) was measured in the atmosphere on samples with coplanar Cr electrodes, using simulated AM 1 solar radiation.

3. RESULTS AND DISCUSSION

The effects of increasing RF power (which determines the substrate bias voltage V_s) on the deposition rate r_D, film composition and electrical behavior is shown in Figs. 1 to 3 for a-Si:H, P-SiO_x and PP-HMDSO, respectively. The Figures show comparisons between the characteristics of films deposited in a "pure" MW discharge, combined MW and RF ("dual" mode) discharges, and also in a pure RF discharge.

In the dual-mode frequency regime, starting from pure MW plasma (V_s=0), and subsequently increasing V_s, the effects on r_D, composition and electrical characteristics are qualitatively similar, so that all three materials can be discussed together: Three regimes of V_s values may be distinguished, suggesting that film growth proceeds via different mechanistic channels:

A: V_s = 0 V; the deposition proceeds in a "pure" MW discharge, with no applied RF power;

B: $0 < V_s < V_{s1}$; the regime of decreasing r_D coincides with low V_s values, resulting from low applied RF power levels;

C: $V_s > V_{s1}$; in this regime of higher V_s values, r_D is seen to rise again.

It is a useful to discuss a growth model involving the following three steps:

i) initiation, or creation of reactive precursors;
ii) propagation, or reactions between precursors;
iii) termination of reactions to produce the final solid reaction product.

The rate and location of these steps in the reactor can be affected separately by changes in plasma parameters, and they are influenced in different ways in MW and RF discharges. In regime A (V_s=0, "pure" MW) the results are, of course, the same as those reported earlier /5-8/. Regime B, when a low value of V_s (or little RF power) is applied, is characterized by a drop in r_D, accompanied by changes in the film composition (see Figures). We surmise that the propagation step is mainly affected by ion-induced desorption of physisorbed surface species. This is accompanied by changes in chemical composition and film morphology, leading to improved electrical properties. In regime C, higher RF energy input and higher V_s result in even more intense energetic surface bombardment; this leads to additional activation of surface sites in the adsorbate, as well as in the gas phase. This is manifested by an upturn in r_D, in important changes in composition, and in further improvements of the electrical properties. For the case of the insulating materials, P-SiO_x and PP-HMDSO, the enhancement of dielectric properties by mixed-frequency deposition has already been discussed briefly elsewhere /9/. Regarding a-Si:H, Paquin et. al. /8/ have reported that "pure" MW deposited films tend to have columnar morphology, and that they age rapidly upon exposure to atmosphere. The result is that their electronic properties are mediocre, R rarely exceeding a few hundred. The present results (see Fig.1) clearly illustrate the beneficial effects of ion bombardment on R, anticipated by Paquin et. al. /8/.

Important morphological changes in the regime of higher energy fluxes were observed by scanning electron microscopy /10/, the films exhibiting a smoother and more densely packed microstructure. The extent of regimes A, B and C are seen to depend on the material being deposited and on the fabrication parameters, such as the pressure and feed gas composition. Applying increasing substrate bias causes similar evolution in the microstructure as with rising substrate temperature /7/; this confirms that V_s and T_s may be considered as interchangeable fabrication parameters, as suggested by the modified structure zone model /11/. The transition from relatively porous to dense structure, we believe, is responsible for the observed changes in electrical properties for all three materials discussed here.

4. CONCLUSIONS

We have demonstrated that the deposition in "dual-frequency" mode plasma leads to selectively controlled film deposition rate, structure and physical properties. This can be accomplished while maintaining high r_D, characteristic of MW plasmas, and without the earlier requirements of elevated substrate temperature, particularly in the case of P-SiO_x and PP-HMDSO.

ACKNOWLEDGEMENTS

This work was funded by the Natural Sciences and Engineering Research Council of Canada, and by the Fonds "Formation des Chercheurs et Aide à la Recherche" of Quebec. The authors are indebted to Dr S. Gujrathi for ERDA measurements, and to Dr O. Küttel for helpful discussions.

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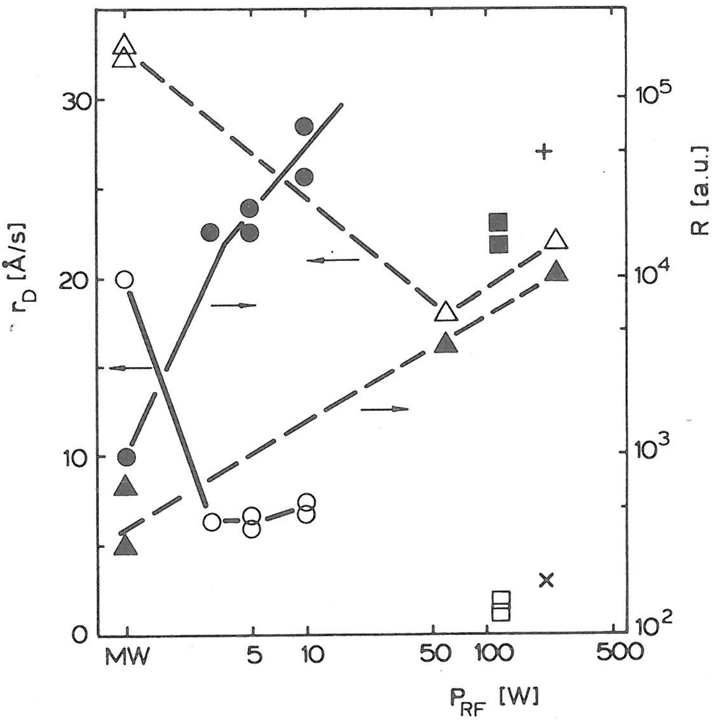

Fig. 1: Effect of RF power input on the deposition rate r_D (○,△) and conductivity ratio R (●,▲) for a-Si:H films deposited from SiH_4 (△,▲) or a SiH_4/Ar (8sccm/42sccm) mixture (○,●). The values for r_D (□,×) and R (■,+) for films deposited in "pure" RF discharge in SiH_4 (+,×) and SiH_4/Ar mixture (□,■) are also shown.

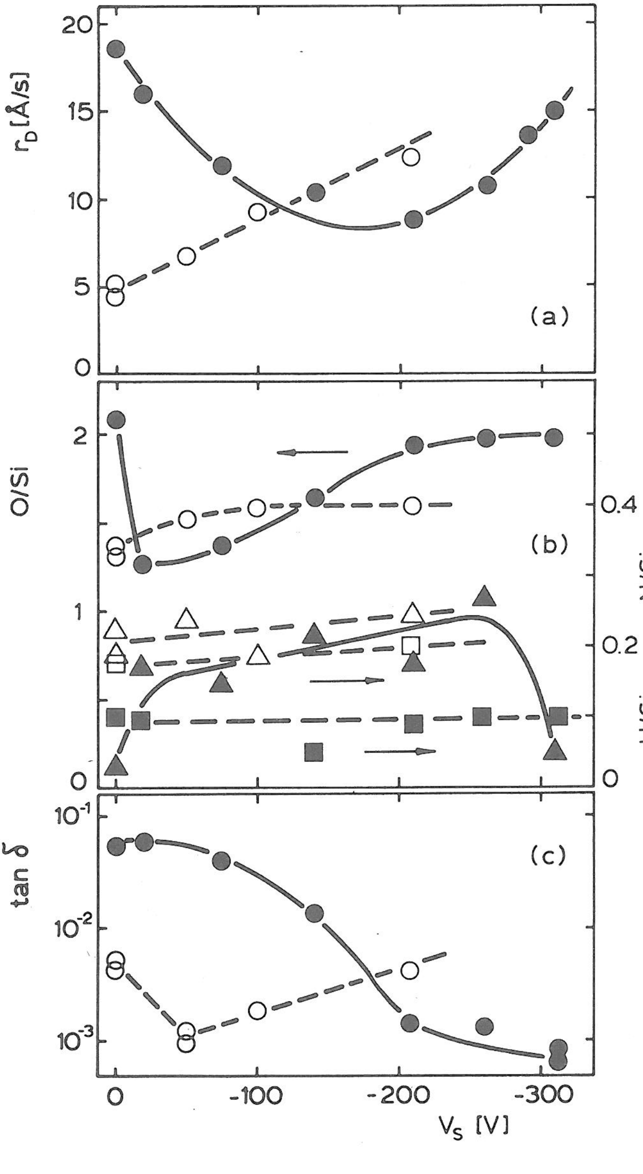

Fig. 2: Effect of the negative substrate bias voltage V_s on the deposition rate r_D (a), atomic concentration ratios O/Si (●,○), N/Si (▲,△), H/Si (■,□) (b), and on the dielectric losses at 1 kHz (c) for P-SiO_x films. Full symbols refer to "dual" mode deposited films, open symbols to "pure" RF deposited films.

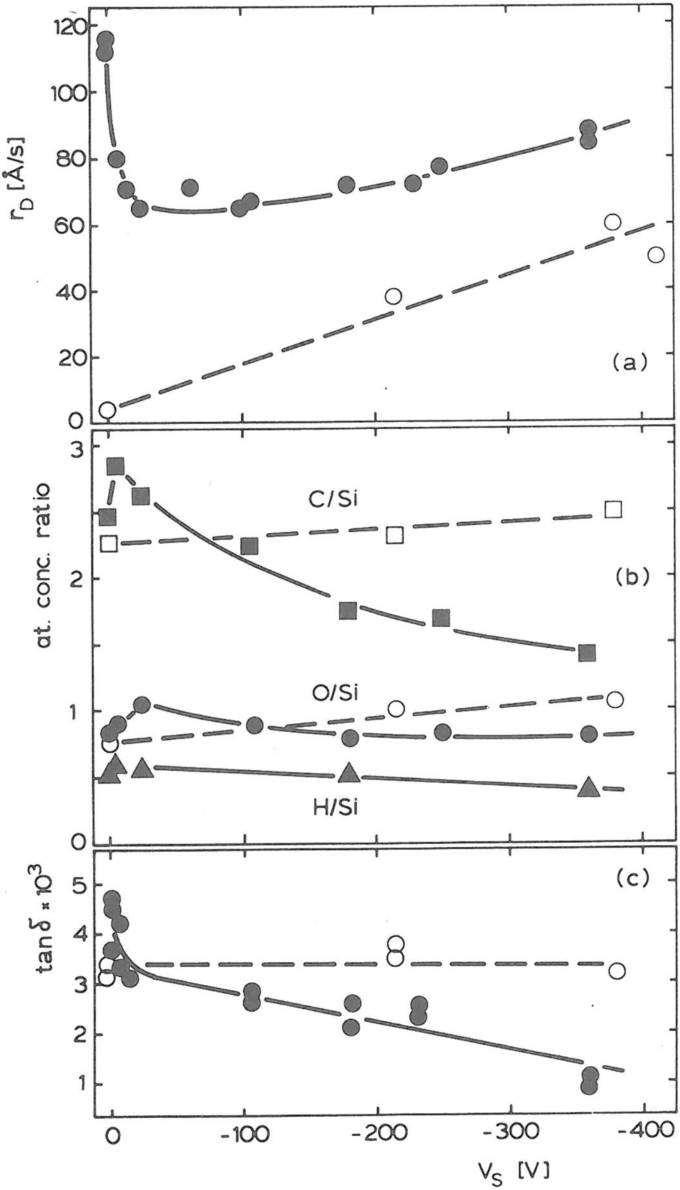

Fig. 3: Effect of the negative substrate bias voltage V_s on the deposition rate r_D (a), atomic concentration ratios: C/Si(■,□), O/Si(●,○), H/Si(▲) (b), and on the dielectric losses at 1 kHz (c) for PP-HMDSO films. Full symbols refer to "dual" mode deposited films, open symbols to "pure" RF depositions.