

THE VACUUM DEPOSITION OF POLYIMIDE LAYERS IN THE PRESENCE OF AN INERT GAS – ANOTHER TECHNOLOGICAL SOLUTION FOR PRODUCING LOW DIELECTRIC CONSTANT MATERIALS

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An investigation of the electrical properties of polyimide thin layers deposited by simultaneous vacuum evaporation of the polyimide precursors in an inert gas argon (Ar) presence in the vacuum chamber has been carried out. It is established that the conductivity of the investigated layers decreases more than six orders of magnitude. The current-voltage characteristics show an improvement of the dielectric properties of the layers with the increased Ar concentration. The observed effects could be related to a growth of the thin polymer layer porosity. This investigation is an attempt to point out how recent developments in the material chemistry may provide novel solutions to the low – k challenge.

Keywords: polyimide, thin organic layers, vacuum deposition, porosity

1. INTRODUCTION

The permanent trend in the microelectronic industry of increasing device densities in the ultra – large scale integrated (ULSI) circuits demands new low dielectric constant (k) materials as an interlayer dielectric (ILD) [1]. Lowering the k value of the ILD decreases the power consumption and reduces the “cross-talk” between nearby interconnects [2, 3]. Polyimides are widely used in the microelectronic industry. Of utmost importance for these microelectronic applications is that polyimides have a low dielectric constant. The development of polyimides with increasingly lower dielectric constant has been the focus of several recent investigations [4 - 6]. The basic strategies used to lower the dielectric constant in the polyimides are [7, 8]:

- incorporating polyimide precursors which minimize the polarizability;
- incorporating fluorine atoms into the polyimide molecular structure;
- incorporating free volumes into the polyimide layer.

The introduction of a free volume in the polymer layers decreases the number of polarizable groups per unit volume resulting in lower values for k_{atomic} and $k_{dipolar}$. The addition of pendant groups, flexible bridging units and bulky groups which limit the chain packing density can all be used to enhance the free volume in polyimides and to reduce the k value respectively [7].

By using an inert background gas nanoporous – carbon (NPC) films [9] of a density $\leq 0,2 \text{ g/cm}^3$ are grown. NPC films are formed using physical processes such as low – power pulsed – laser deposition with attenuation of the ablated carbon

species kinetic energy attained by using a noble gas – Ar, limiting the free paths of the clusters. These results could be related to our investigations. In our previous studies [10, 11] we have established the strong influence of the preparation conditions on the control of the k values. An investigation of the electrical properties of the polyimide thin layers, deposited by simultaneous vacuum evaporation of the polyimide precursors - 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) in the noble gas Ar presence in the vacuum chamber has been carried out. This is the objective of the present paper – to demonstrate another possibility for creating of a type of new low k materials by creation of conditions for formation of nano-porosity in well-known dielectric layers - polyimides.

2. EXPERIMENTAL SET – UP

2.1. Grounds for the choice of experimental conditions

If at the time of the vacuum deposition of the polyimide precursors, conditions for incorporation of the inert gas in the layer volumes could be accomplished, then under the conditions of their imminent thermal treatment [5] to the production of the polyimide, the gas should be desorbed and free volumes could be obtained. The porosity of the produced films would be depending on the balance between the inert gas pressure [9] and the deposition rate. A reasonable compromise should be sought because the evaporation process is hampered by the augmented pressure thus resulting in the formation of undesired defects in the layers. Also, the increased porosity would lead to an improvement of the dielectric properties of the obtained layers which is the aim of the experiments carried out by us.

2.2. Sample preparation

The vacuum deposited polyimide (VDP) films were prepared on soda-lime-glass plates. The vacuum chamber was evacuated by oil diffusion pump to a pressure of $< 7 \times 10^{-4}$ Pa. The precursors used PMDA and ODA, were supplied by *Merck* and stored in the dark. They were evaporated from two independent thermally-heated Knudsen type evaporation sources (Fig.1.). The evaporation temperatures were 120-145°C for PMDA and 100-110°C for ODA used in order to achieve deposition rates from 0.2 to 2 Å/sec, the latter being carefully controlled by quartz oscillators. Thus, the optimal ratio in the flux of 1:1 for the ODA : PMDA vapours was ensured. The process of maintenance of a definite permanent residual pressure of the inert gas in the vacuum chamber was performed by the introduction of the corresponding gas by a mass flow controller which is computer-controlled via information obtained from the vacuum meter. The precursors condensed on the substrates in the presence of Ar atmosphere at vacuum $4 \cdot 10^{-3}$ and $4 \cdot 10^{-2}$ Pa. Thus the mixed (precursors-Ar) films were built-up.

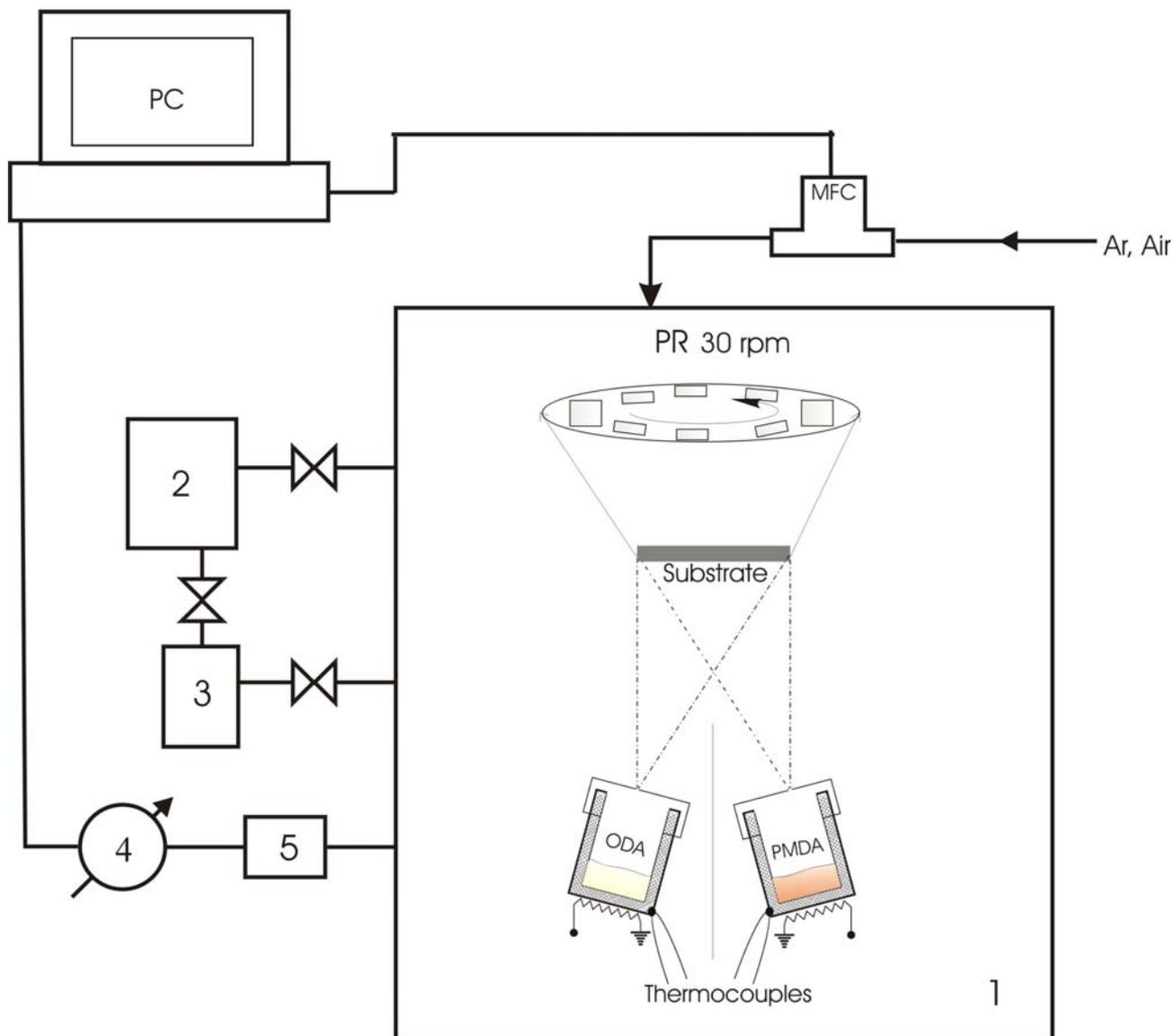


Fig.1. Experimental set-up for polyimide sample formation: MFC – Mass Flow Controller; PC – Personal Computer; 1 - vacuum chamber; 2 - diffusion pump; 3 - forvacuum pump; 4 - vacuum meter; 5 - high vacuum gauge.

The co-deposited precursor layers were transformed into polyimide films by a two - step thermal treatment at strictly controlled temperatures (1 hour at 170°C followed by 1 hour at 250°C). The thermal treatment conditions determine the degree of imidization, i.e. the degree of interactions between ODA and PMDA, which result in formation of the polyimide, 280 nm thick films. Also, as could be expected by increasing the temperature the incorporated Ar should be desorbed from the layers and free volumes should be formed.

2.3. Electrical measurements

The investigated polyimide layers were evaporated on soda – lime glass substrates with previously prepared bottom gold electrodes. An aluminum top electrode was then vacuum evaporated. The resulting Au / PI / Al sandwich structures were again thermally treated at 200°C for 4 hrs to make the metal / polymer contacts more effective. Current-voltage (I-V) characteristics were measured in DC (Direct Current) mode at room temperature in vacuum of 1 Pa by computer controlled Keithley 617 electrometer. The conductivity σ was calculated using the Equation (1):

$$\sigma = \frac{\Sigma \cdot d}{S} \quad (1),$$

where S is the sample area and d is the layer thickness. The conductance Σ was determined as the slope of the linear regression of the ohmic part of the I-V curves.

3. RESULTS

Typical I-V curve for vacuum deposited polyimide in an atmosphere without Ar is presented in Fig. 2. The curve consists of two parts. The ohmic part at the beginning of the curve is due to the thermally generated free charge carriers. The steep part of the characteristic in case of high voltages is due to the strong injection of the electrodes. The calculated σ is $1.9 \times 10^{-7} \text{ ohm}^{-1} \text{ m}^{-1}$.

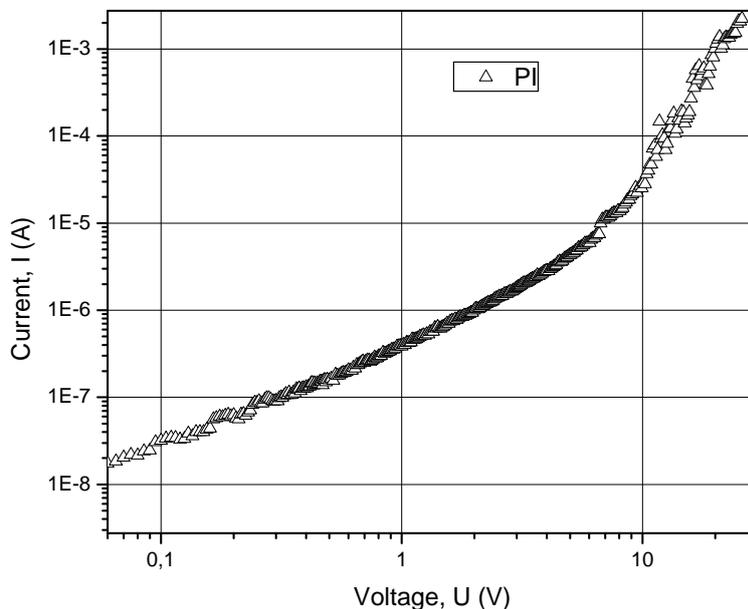


Fig. 2. Current-voltage characteristic of 280 nm thick polyimide layer, obtained in a vacuum of 7×10^{-4} Pa and thermally treated after the deposition

The influence of the Ar on the film resistivity is shown by comparing the ohmic parts of the I-V characteristics in Fig. 3. The current-voltage characteristics show an improvement of the dielectric properties (increased resistance) of the layers with an increasing Ar concentration. The difference between the resistance values of the two Ar concentrations (curve 2 and 3) is insignificant. Most probably saturation at a pressure of $\sim 10^{-3}$ Pa Ar is reached.

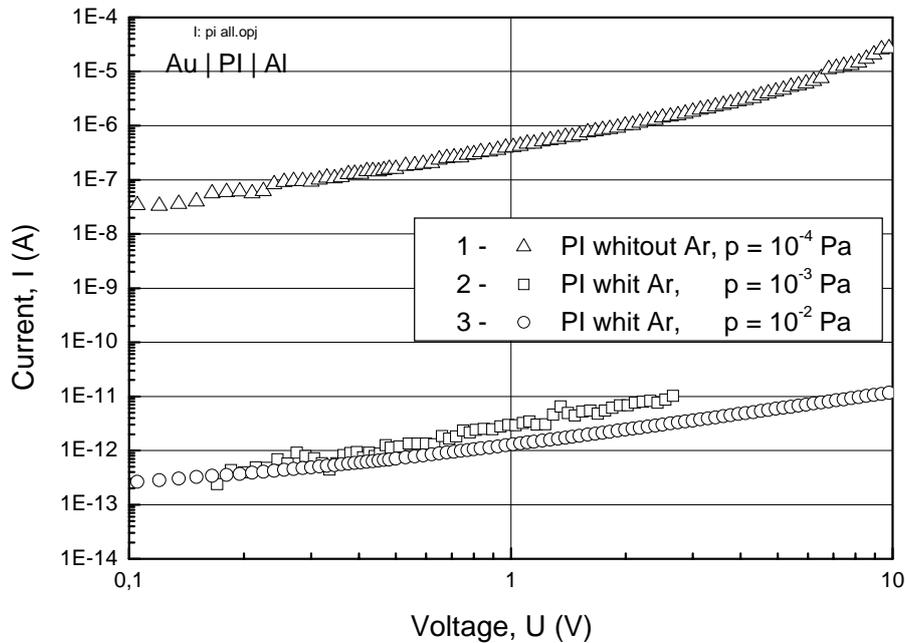


Fig. 3. The ohmic current depending on the gas atmosphere of thermally treated 280 nm thick PI layers: 1- without Ar; 2 and 3 with Ar

The calculated σ from the presented curves are summarized in Table 1. It could be seen that the conductivity of the investigated layers (obtained in an Ar atmosphere) decreases more than six orders of magnitude (from $1.9 \times 10^{-7} \text{ ohm}^{-1} \text{ m}^{-1}$ to $7.0 \times 10^{-14} \text{ ohm}^{-1} \text{ m}^{-1}$).

Table1: Summarized results from the electrical measurements of VD layers (280 nm thick) of different types

N	VD Layer type	Vacuum [Pa]	Conductance (Σ) [ohm ⁻¹]	Conductivity (σ) [ohm ⁻¹ m ⁻¹]
1	without Ar	10 ⁻⁴	3x10 ⁻⁷	1.9x10 ⁻⁸
2	with Ar	10 ⁻³	2.5x10 ⁻¹²	1.4x10 ⁻¹³
3	with Ar	10 ⁻²	1.2x10 ⁻¹²	7.0x10 ⁻¹⁴

It was also found that the layers possess a lower (20%) dielectric constant compared to the standard samples. This effect could be related to an increase of the thin polymer layer porosity. The latter, according to our suggestion is a consequence of the gas cavities formed in the volume.

4. CONCLUSION

By controlling the processing conditions pores of nanometer dimensions can be formed. The research interest in porous materials is connected with the possibility for controlling the thin layer polyimide matrix so that it could influence their electrical properties. This allows for tailoring the conductivity properties of the vacuum deposited polymer layers.

This investigation is an attempt to point out how recent developments in the material chemistry may provide novel solutions to the low – k challenge.

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