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ELECTRICAL PROPERTIES OF A THIN LAYER POLYIMIDE MATRIX

V. Strijkova[*], D. Dimov, A. Paskaleva[a], I. Zhivkov, E. Spassova, J. Assa, G. Danev

Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., bl. 109, 1113 Sofia, Bulgaria
[a]Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Tzarigradsko Chaussee 72, 1784 Sofia, Bulgaria

Polyimide thin layers (500 nm) have been prepared by vacuum co-deposition of 4, 4'- oxidianiline and pyromellitic dianhydride precursors followed by thermal treatment. The dielectric properties of the samples are evaluated by C-V and I-V measurements. It has been shown that the vacuum deposited polyimide matrix displays attractive dielectric properties: $\varepsilon < 3$ and low leakage currents. The influence of the technological pre-history on the electrical properties of the layers has been discussed.

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1. Introduction

Polyimides (PIs) are organic materials with an attractive combination of characteristics (low *k*, good thermal stability, chemical inertness and good adhesion to semiconductors and metals) for the science and the electronic industry [1-3]. PIs have been widely applied as dielectric and packaging materials in microelectronics, as a waveguide in optoelectronics because the use of PI as *a* low – *k* material (*k* denotes the relative permitivity, w*h*ich is often also symbolized by ε) can considerably reduce the resistance-capacitance (RC) time delays, cross-talks and power dissipation in the new generations of integrated circuits [4,5]. At the same time PI is a very suitable material for matrices in the nanocomposite systems where the composite properties can be tailored changing the "guest" concentration or "guest" particle size [6,7]. The investigations of these materials provide a new approach, in particular, in the field of the so-called organic material electronics. Obviously information about the electrical properties of PIs is required.

We have focused our investigations on the electrical properties of vacuum deposited polyimide (VDP) as they are very sensitive to variations in the polyimide layer quality and electrical measurements are especially suitable for the characterization of VDP layers. The aim of the paper is to show the influence of the PI matrix technological pre-history (deposition conditions) on the electrical properties of the layers.

2. Experimental

2.1. Sample preparation

The PI layer matrix (500 nm thick) was formed by vacuum co-deposition of precursors 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) from two independent thermally heated Knudsen-type vessel sources. The base pressure was $\leq 5 \times 10^{-4}$ Pa. The evaporation

[*]Corresponding author: vily@clf.bas.bg

temperatures were 120 – 145 °C for PMDA and 100 – 110 °C for ODA. The deposition rates, controlled by quartz oscillators, were 0,2 to 2 Å/s. Four different samples were prepared:
1. PI layer matrix formed on planetary rotating (PR) substrates (30 rpm). The films on the PR substrates were continuously grown [6].
2. PI layer matrix formed on linearly moving (LM) substrates (fixed rates of 5 mm/s). The films were built up via layer-by-layer formation.
3. PI layer matrix formed by means of energy-stimulated processes based on electron-assisted deposition (EAD) in vacuum: U_k = 12 V; U_a = 4,5 kV [8].
4. Composite layers (PI/ CuPc) with a "guest"- copper phthalocyanine in the matrix volume 15%, LM substrates. Particles of CuPc were evaporated from a Knudsen vessel, deposition rate 11 Å/s [6].

The VD layers (samples 1-3) were transformed into PI by a two-step thermal treatment - 1 hour at 170 °C followed by 1 hour at 300 °C, in air [3]. The samples 4 were thermally treated for 1 h at 200 °C - the optimal conditions for good quality of the composite layers [6].

2.2. Method of investigation

The electrical measurements were performed at a frequency of 1 MHz with a Hewlett Packard Digital LCR meter 4271B with an amplitude ranging from 0.2 to 1.0 V.

The substrates used for the electrical measurements [9] were p-type (100) Si wafers B doped to $N_A \approx 5.10^{15}$ cm^{-3}. Prior to deposition they were cleaned using a chemical cleaning procedure. On top of the PI 500 nm of Al was deposited for contacts. It was found that the Al adhesion to PI films was not very good. Therefore, for most of the samples Ti was used as an adhesion layer. Ohmic contacts to the reverse side of the wafers were accomplished by depositing of a 500 nm Al layer.

3. Results and discussion

The results obtained for ε (Table 1 – sample 1 and 2) show an influence of the dynamic state of the substrate during the layer formation. For LM type of deposition there exist larger possibilities for uncontrolled impurity absorption from the residual atmosphere in the vacuum chamber. In this case ε displays higher value. For the PR type of deposition, the growth of the layer is continuous and a probability for incorporation of "free volumes" exists. As a consequence, the ε become smaller values.

Table 1. Summarized results from the electrical measurements of VD layers of different types.

No.	VD layer type	Thickness (d) [nm]	Capacitance (C) [pF]	Dielectric constant (ε)
1	VDP layer on Planetary rotating (PR) substrate	500	9	2.02
2	VDP layer on Linearly moving (LM) substrate	490	11	2.40
3	VDP layer with Electron-assisted deposition (EAD) on LM substrate	430	14	2.70
4	Composite PI/CuPc	600	12	3.20

In Fig. 1 the I-V curves of samples 2,3 and 4 (from the Table 1) are presented. The curves' shapes of 2 and 3 are similar indicating that a similar conduction mechanism governs the current in both samples. However, the current in sample 3 is *a* half to one order of magnitude lower (depending on the voltage) compared to sample 2, i.e. layers obtained by EAD are less leaky than the layers which are not subjected to electron bombardment during deposition. This fact implies that the influence of electrons on the film structure is beneficial in terms of leakage current (an important factor for the electrical property of the low-*k* interlayer dielectric film). There are two processes which could account for the lower leakage current in the sample 3:

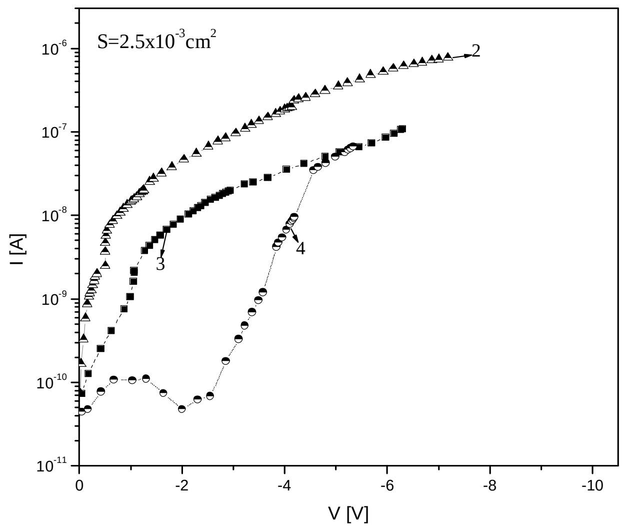

Fig. 1. I-V characteristics of thin VD layers: 2- PI layer formed on LM substrates; 3- PI layer formed on LM substrates by means of EAD; 4- Composite layer (PI/ CuPc).

1) probability for C nanocluster formation in the PI matrix as a result of bond breakage by the electrons. As a consequence a composite material with *a* higher dielectric constant is formed (Table 1, sample 3). Our previous investigations [10] of composites, when C particles are incorporated by means of quasi-arc evaporation and erosion of the graphite electrode in the course of the PI layer growth show that the conductivity is considerably dependent on the C amount;

2) the influence of the electrons does not cause any change of the structure, but results in annealing of defects and formation of a layer with less non-perfections. This is implied by the observed densification of the layer, i.e. the reduction of the film thickness and accompanying increase of the dielectric constant. Therefore, both processes can cause the observed decrease of the leakage current as well as the increase of the dielectric constant in the case of electron irradiation. Moreover, both processes can occur simultaneously and at this stage of the investigations it is not possible to assert whether some of them play a dominant role.

The FTIR spectroscopy investigation [11] of the composite layers (PI/CuPc) does not give indications of a chemical interaction between the thin layer matrix and the “guest” which is expressed in the absence of peaks in the spectra that would account for the emergence of new bonds.

Sample 4 exhibits quite a different I-V behavior. No significant conductivity is observed up to about –3 V. The current is below 10^{-10} A and is mainly due to the displacement current. So, in the low field region this sample shows up to three orders of magnitude lower leakage current compared to the sample 3. Above –3 V the current increases steeply and at about – 5 V it is already equal to the current in sample 3. Therefore, the embedding of CuPc in the PI matrix results in a distinct change of the conductivity in the film and a higher ε (3.2 – Table 1).

4. Conclusion

The dielectric properties of polyimide thin layers are evaluated on capacitors using C-V and I-V measurements. The following conclusions could be drawn from the results presented. The VDP matrix displays good dielectric properties: ε < 3 and low leakage currents. The dynamic state of the substrate during layer formation influences the layer quality, hence its permittivity – the layers obtained with planetary rotating substrate exhibit lower permittivity. The influence of the PI matrix technological pre-history on the electrical properties of the layers is demonstrated. The VDP layers obtained with electron assisted deposition reveal lower leakage current and slightly higher permittivity that could be due to structural changes and/or annealing of defects. The embedding of CuPc in the PI matrix results in significant decrease of leakage current – up to three orders of magnitude. The characteristic of low leakage current is proper to a superior interlayer dielectric film.

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