

Influence of the residual gas atmosphere in the vacuum chamber on the properties of thin polyimide layers.

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Thin polyimide (PI) layers prepared by simultaneous vacuum evaporation of the polyimide precursors in presence of gas were investigated. After deposition, the layers were transformed into PI by thermal treatment. This study discusses the influence of the gas atmosphere of Ar, N₂, He or air in the vacuum chamber on the imidization process, electrical properties and microhardness of the layers. Infrared spectra of these samples were recorded and studied. Our investigation has shown that the gas type has a significant influence on the electrical and micromechanical properties of the layers. The most significant changes in the electrical and micromechanical properties were found for polyimide layers obtained in the presence of nitrogen gas in vacuum chamber. These layers display the highest values of the microhardness, the highest degree of imidization and the lowest value of the capacitance.

Keywords: polyimide layers; vacuum deposition, electrical properties and microhardness

INTRODUCTION

Aromatic polyimides (PIs) demonstrate good material characteristics such as high thermal stability, good mechanical strength, low dielectric constant, high chemical resistance, high optical transmittance [1]. Polyimides are widely used in the microelectronic industry as insulators, barrier layers or capsulation layers [2, 3]. One of the methods used for PI layer preparation is physical vapor deposition (PVD) of precursors, like diamines and dianhydrides [4] followed by a thermal treatment.

The thin vacuum deposited polyimide layers show an uniform and easy to control thickness, a lower dielectric constant as compared to layers prepared by spin coating and do not contain a solvent [1, 5]. Their structure, electrical and optical properties and microhardness strongly depend on the preparation conditions [1].

The gas introduction into the evaporation chamber reduces the total pressure and the inert gas is inevitably buried into the growing film, which may change some of the film properties.

The aim of this investigation is to study the influence of the residual gas atmosphere of Ar, N₂, He or Air in the vacuum chamber on the degree of

imidization, electrical properties and microhardness of thin polyimide layers deposited by vacuum evaporation in the presence of gas. The influence of the type of gas in the vacuum chamber on these properties is also studied.

EXPERIMENTAL

The layers were obtained by vacuum deposition of the precursors – oxydianiline (ODA) and pyromellitic dianhydride (PMDA). They were evaporated from two independent thermally heated Knudsen type evaporation sources. 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 [6]. The Polyimide (PI) layers were prepared by using of planetary movement of the substrates of soda-lime-glass plates or p-type (100) Si wafers, in vacuum system UVN. The process of maintenance of a definite permanent residual pressure of the 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 vacuummeter. The precursors condensed on the substrates in the presence of residual gas

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atmosphere at vacuum of 10^{-2} Pa. The co-deposited precursors layers were transformed into PI layer by two steps thermal treatment for 1 hour at 170°C and for 1 hour at 250°C . The goal of the thermal treatment is to accelerate the polycondensation solid state reaction between the monomers, leading to the PI formation [1]. In addition to the imide formation, polyamic acid (PAA) as an intermediate product, may also undergo either cyclization to form iso-imide or, by reversible dissociation, to regenerate the anhydride and the amino groups [1]. The possible types of chemical defects include also trapped monomers, trapped polyamic acid, amide or imine bond formation [1].

After the thermal treatment, layers with thickness of 300 nm and 1000 nm were produced. Thickness of the PI layers was measured using profilometer Talystep. FTIR- spectra of PI layers deposited on KBr substrate were recorded by a Perkin Elmer 1600 spectrometer in the $2000\text{--}650\text{ cm}^{-1}$ range with resolution of 4 cm^{-1} and interval of 0,2. The peak at 1501 cm^{-1} characterizes p-substituted benzene rings. It is used as an internal standard and does not change at the imidization time. That is why the degree of imidization (δ) can be indirectly defined by the ratio of the absorptions (the corrected areas of the bands) 1380 cm^{-1} to 1501 cm^{-1} [7]. The degree of imidization is of essential importance for most of the film properties. For electrical measurements, the PI layers were deposited on Si wafers. The Al top electrode was the vacuum evaporated thought mask. The capacitance was measured at frequency $f=1\text{MHz}$, room temperature $t = 20^{\circ}\text{C}$ and 40% relative humidity by Resonance method. The capacitance on the Si/PI/Al sandwich structures was measured by RLC meter ASSIKO - 02 with automatic calibration of zero. Error range of 2 nF capacitance measurement 0.1% of the measured value. The layer microhardness (Mhd) was determined by the Knoop prism method known to be sensitive for measurements of thin layers [8]. The load value was 1.25 mPa for all samples studied.

RESULTS AND DISCUSSION

FTIR spectra of the thermally treated PI layers deposited in presence at different gas –air, Ar, N_2 or He atmosphere are presented in Fig.1. As it is seen the reduced intensity of the absorption bands near 1550 cm^{-1} (amide II) and 1665 cm^{-1} (amide I)

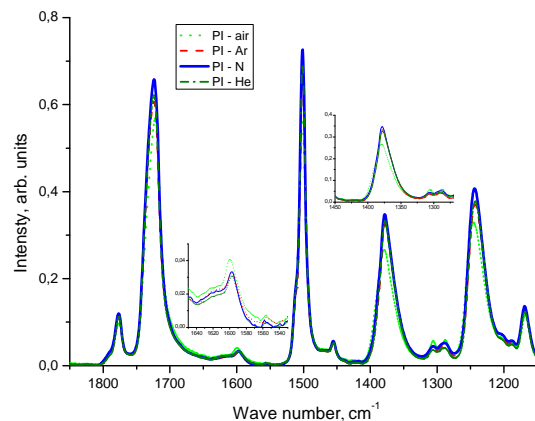


Fig. 1. FTIR spectra of 1000 nm thick polyimide layers obtained at residual gas atmosphere of air, Ar, N_2 , and He.

indicates that polyamic acid has been converted into PI. Simultaneously, this is confirmed by the occurrence of the C=O stretch (imide I) peaks at $1770\text{--}1780\text{ cm}^{-1}$ (symmetric), $1720\text{--}1740\text{ cm}^{-1}$ (asymmetric) and the typical C–N stretch (imide II) peak around 1380 cm^{-1} . The intensity of the anhydride peak around 1300 cm^{-1} and the intensity of the imine (NH_2) peak around 1600 cm^{-1} and 1550 cm^{-1} increase for layer produced in air residual atmosphere. The peaks at 1290 cm^{-1} and 1304 cm^{-1} are due to friable matrix in this case and due to ODA conformations – more degrees of freedom in achieving the required orientation (the two benzene rings are twisted one with respect to the other). Layers produced in nitrogen residual atmosphere are with lower amount of by-products. Fig. 2 shows

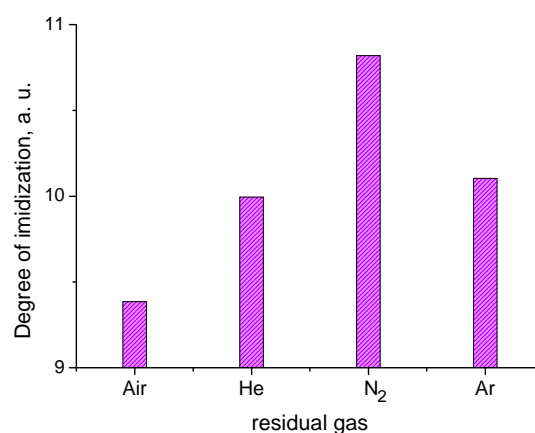


Fig. 2. Degree of imidization of the polyimide layers with thickness 1000 nm obtained at residual gas atmosphere of air, Ar, N_2 , and He.

the degree of imidization in dependence of the type of the residual gas. The peak around 1380 cm^{-1} indicative of imide formation was used for assessing the degree of imidization. The layer produced in nitrogen atmosphere is with the highest degree of imidization. The degree of imidization decreases with about 10% for layers deposited in presence of air compared with the layers produced in presence of nitrogen (Fig.2). The results obtained indicated that layers obtained in the presence of an inert gas – Ar, He or N_2 have higher degree of imidization. The rate of imidization depends on the availability of favorable conformation for cyclodehydration of amic acid to imide. PVD involves a solid-state polymerization that, in the absence of solvent, is kinetically hindered due to low monomer and oligomer mobility [9]. The presence of the nitrogen most probably leads to favorable conformations affording the highest degree of imidization.

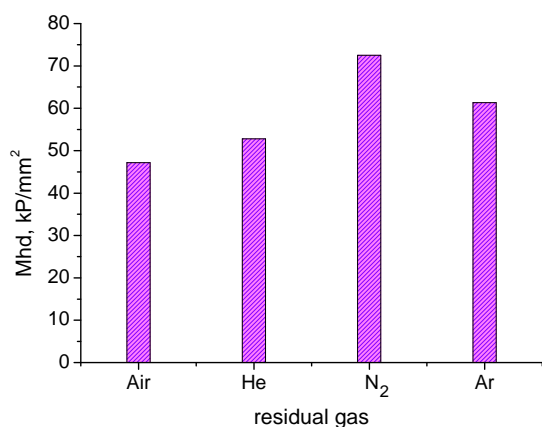


Fig. 3. Microhardness of the 1000 nm thick polyimide layers deposited at different residual gas atmosphere.

Fig. 3 summarizes results from the microhardness measurements of the 1000 nm thick polyimide layers deposited at different residual gas. The layers obtained in the presence of nitrogen have the highest value of microhardness. Most probably this is due to their increased degree of imidization. As known the high degree of imidization leads to the formation of longer polymer chains and appearing of inter-chain forces resulting in increased film density.

The influence of the presence of residual gases in vacuum chamber during the deposition of the layers on their dielectric properties was investigated by measurement capacitance of the structures Si/PI/Al. Thickness of the PI layers was 300 nm. Fig.4

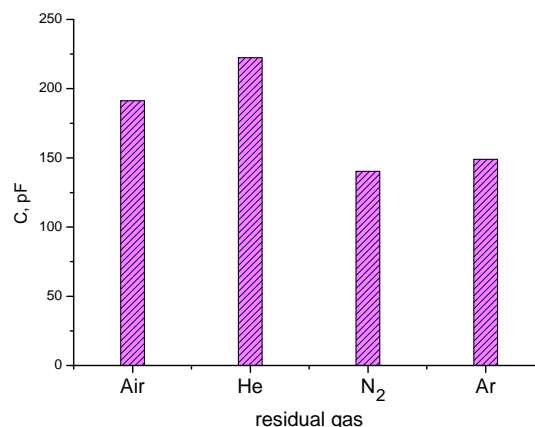


Fig. 4. Capacitance of the 300 nm thick polyimide layers deposited at different residual gas atmosphere.

shows the capacitance of the PI layers deposited at indicated residual gas. It is seen that the lowest value of the capacitance have layers obtained in a nitrogen atmosphere in the vacuum chamber. As it is known the high degree of imidization leads to low values of the dielectric constant and therefore to low values of their capacitance. From this point of view the result obtained is consistent with the highest degree of imidization derived by FTIR spectra of the same layers.

CONCLUSION

The results show that the controlled introduction of different gas into the vacuum chamber causes a change in the electrical and micromechanical properties of the PI layers. The most significant changes in these properties were found for polyimide layers obtained in the presence of nitrogen atmosphere. These layers display the highest values of the microhardness, the highest degree of imidization and the lowest value of the capacitance and hence dielectric constant.

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ВЛИЯНИЕ НА ОСТАТЪЧНАТА ГАЗОВАТА АТМОСФЕРА ВЪВ ВАКУУМНАТА КАМЕРА ВЪРХУ СВОЙСТВАТА НА ТЪНКИ ПОЛИИМИДНИ СЛОЕВЕ

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(Резюме)

Изследвани са тънки полиамидни (PI) слоеве, получени чрез съвместно вакуумно съизпарение на изходните прекурсори в присъствие на газ. След отлагане, слоевете бяха подложени на термично третиране. Това изследване разглежда влиянието на остатъчната атмосфера от различен газ, Ar, N₂, He или въздух, във вакуумна камера, върху степента на имидизация, електричните свойства и микротвърдостта на слоевете. Получените резултати показват, че вида на газа има значително влияние върху електрическите и микромеханичните свойства на слоевете. Най-съществени промени в тези свойства са установени за полиамидни слоеве, получени в присъствието на азотна атмосфера. Тези слоеве показват най-висока стойност на микротвърдостта, най-висока степен на имидизация, най-ниска стойност на капацитета, т.е. на диелектричната константа.