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LEAD ZIRCONATE TITANATE ON BASE METAL FOILS: AN APPROACH FOR EMBEDDED HIGH-*K* PASSIVE COMPONENTS*

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Lead Zirconate Titanate thin films on base-metal foils: An approach for embedded high-*K* passive components

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ABSTRACT

An approach for embedding high-*K* dielectric thin films into polymer packages has been developed. $Pb_{0.85}La_{0.15}(Zr_{0.52}Ti_{0.48})_{0.96}O_3$ thin films were prepared by chemical solution deposition on 50 μm thick Ni-coated Cu foils. Sputter deposited Ni top electrodes completed the all base-metal capacitor stack. After high temperature N_2 crystallization anneals, the PLZT composition showed reduction resistance while the base-metal foils remained flexible. Capacitance density and Loss tangent values range between 300 and 400 nF/cm^2 and 0.01 and 0.02 from 1 to 1000 kHz respectively. These properties represent a 2 to 3 order of magnitude improvement over available embedded capacitor technologies for polymeric packages.[1]

INTRODUCTION

Embedding thin film high-permittivity dielectrics into low temperature processed polymer packages offers advantages in electronics miniaturization and manufacturing cost reduction. Miniaturization potential stems from replacement of surface mount components and the subsequent reduction of the required wiring board real estate. Cost reductions are associated with the ability to produce packaging substrates with capacitive layers pre-embedded. Such layers remove the need for pick-and-place assembly operations which can comprise an appreciable fraction of the manufacturing cost.[1] Photolithographic methods coupled with etching and metallization steps can conceivably be used synthesize the necessary combinations of capacitive elements and interconnects rapidly and in large quantity.

We present here a strategy to produce high permittivity capacitive layers compatible with low temperature processed polymer packages. To avoid traditional temperature limitations, all high temperature processing steps required by the oxide dielectric would be performed prior to the embedding process. This goal was achieved through film deposition onto metal foils which could be subsequently embedded using standard lamination methods. Unlike other commonly used substrates, metal foils are thin enough as not to add appreciable thickness to the subsequent package. Such metal foils are, however, thick enough to support the brittle as deposited oxides. In this study, composite base metal foils (comprised of 50 μm Cu coated with 4 μm of electroless Ni) were used as the carrier substrates to minimize cost. This work follows several previous investigations of high-*K* films on metal foils, and/or with base-metal electrodes.[2-7]

La-doped $Pb(Zr,Ti)O_3$ was used as the high permittivity dielectric. The La doping drives the Curie transition below room temperature leaving a large *K* and non-hysteritic electrical properties. This composition is tolerant of the non-stoichiometry expected after processing in the inert atmospheres required to preserve the base metal foil. Resulting oxygen vacancy populations can be ionically compensated by controlled Pb-deficiency.

EXPERIMENTAL PROCEDURE

50 μm thick Cu-foil substrates (0.5 oz. gage) were obtained from Motorola. 4 μm of autocatalytic (i.e., electroless) Ni (abbreviated as e-Ni) was deposited on each side of the metal foil by MacDermid Inc. from a $NiCl_2$ - $Na(H_2PO_2)^-$ solution bath. The foils were obtained in 12 " x 14" sheets. Sections of foil 2.5 cm x 5 cm were cut from the large sheets and used as the standard substrate size. Prior to depositions, the foils were cleaned by rinsing in acetone and isopropanol. AFM surface imaging of the as-received foils revealed ~ 2 μm rms roughness, with 1-3 μm diameter e-Ni clusters.

PLZT was prepared by chemical solution deposition. The precursor solution was methanol-based, incorporating lead acetate trihydrate, titanium isopropoxide, lanthanum isopropoxide, and zirconium N-butoxide chemical sources.[8] After spin-on deposition, the films were dried on a hot plate at 250 °C for 5 min, then pyrolyzed in air @ 450 °C (tube furnace) for 10 minutes. This procedure was

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repeated 6 times to achieve the desired thickness of ~ 6000 Å. After deposition, drying, and pyrolysis, the films were crystallized in an N_2 tube furnace at 600 °C for 30 minutes. Capacitor structures were completed by ion beam deposition of Pt or Ni top electrodes.

The film surface topography, crystallinity, and microstructure, were characterized using atomic force microscopy, X-ray diffraction, and transmission electron microscopy. Frequency and electric field dependent dielectric properties were measured using an HP 4192A impedance analyzer.

RESULTS AND DISCUSSION

Fig. 1 shows an θ-2θ x-ray diffraction pattern respective of thin film PLZT samples deposited on e-Ni substrates under the optimized processing conditions. As seen in the figure, peaks are present from Ni, Cu, Ni_3P, and PLZT. Under the optimal processing conditions, no evidence is found suggesting the presence of pyrochlore crystals. It is also apparent from the diffraction pattern that the reducing anneal conditions are effective in preventing oxide formation in the composite base metal foil. The Ni_3P phase forms via a precipitation reaction in the as-deposited e-Ni which contains between 9 and 11% dissolved phosphorus.[9]

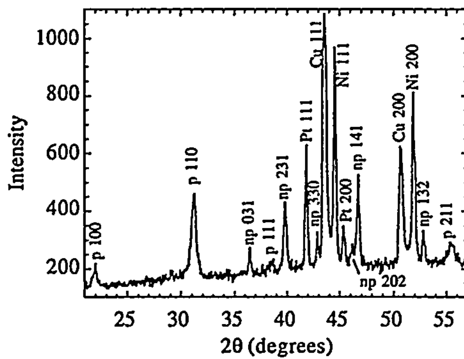

Fig. 1: θ-2θ x-ray diffraction pattern of 6 layer (~6000 Å thick) PLZT thin film deposited on an e-Ni coated foil substrate. In the figure, p = perovskite PLZT, np = Ni_3P, and Pt refers reflections from Pt top electrodes.

Of some concern was the large surface roughness of the as-received e-Ni surfaces (~ 10 x greater than the dielectric thickness). The large undulations could potentially lead to shorting or premature electrical breakdown. AFM analysis was performed on the final PLZT thin films, a typical result is given in Fig. 2.

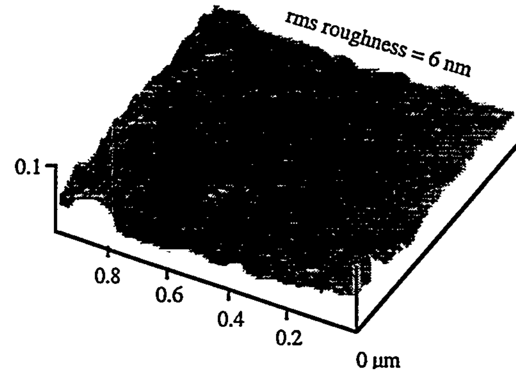

Fig. 2: Tapping mode AFM image of 6 layer (~6000 Å thick) PLZT thin film deposited on an e-Ni coated foil substrate.

Note that on the scale of this image, the surface appears quite smooth. If, however, an image is taken over a larger area (10 μm x 10 μm), the roughness is similar to that of the e-Ni substrate prior to deposition, i.e., ~ 2μm rms. This surface topography suggests a typical lateral grain size between 20 and 100 nm, and relatively conformal coverage.

In this report, electrical characterization is limited to room temperature measurements. Fig. 3 shows a capacitance-voltage curve typical of the PLZT: the non-hysteritic response indicates the effectiveness of La-doping to temperature-shift the ferroelectric transition below room temperature.

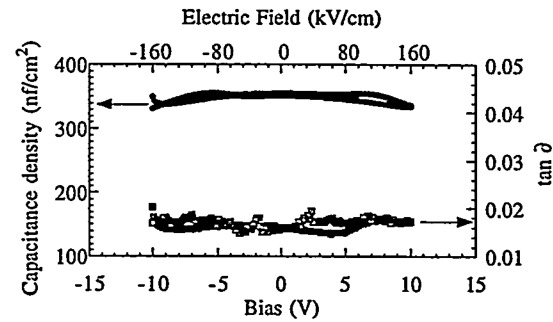

Fig. 3: Voltage dependence of the permittivity and dielectric loss tangent for a 6 layer (~6000 Å thick) PLZT thin film deposited on an e-Ni coated foil substrate.

Fig. 3 also demonstrates the limited dielectric tunability - the combination of a small grain size and relatively low-temperature processing likely contributes to this condition. (The lack of tunability is desired for the targeted applications.)

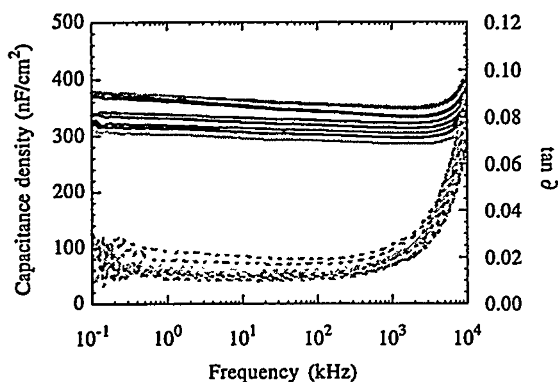

Fig. 4: Frequency dependence of the permittivity and dielectric loss tangent for a 6 layer (~6000 Å thick) PLZT thin film deposited on an e-Ni coated Cu foil substrate.

Fig. 4 gives the frequency dependence of the permittivity and loss tangent for a typical PLZT sample. In Fig. 4, 10 curves are given and indicate the degree of variability among test capacitor structures. Typically, the yield of functional capacitors (500 μm diameter circles defined with a shadow mask) is ~80 %. This data is presented as capacitance/unit area since these units can be readily compared to other capacitor technologies. (The average dielectric constant at 10 kHz was 240.) The dielectric constant was found to drop approximately 1 % per decade.

One likely influence producing the relatively low dielectric constant of this PLZT (when compared to bulk values exceeding 10,000)[10] is the formation of a low-permittivity layer at the PLZT / e–Ni interface. Cross-sectional TEM images were taken to investigate this possibility, Fig. 5 gives the result. In this image an interfacial layer between 35 and 40 nm in thickness becomes apparent.

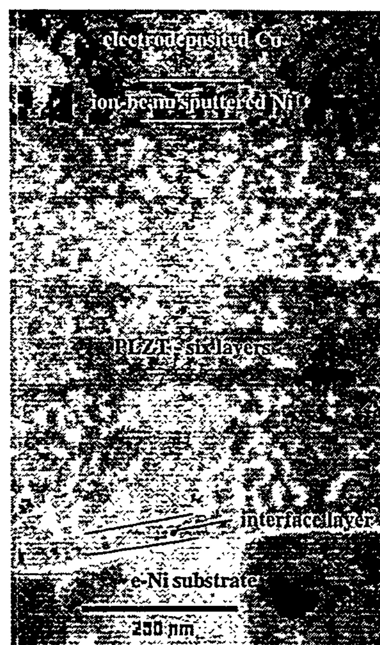

Fig. 5: Cross-sectional TEM image of a foil-based capacitor detailing the dielectric layers and interface formation between PLZT and e-Ni bottom electrode.

At this point it remains unclear as to the exact composition of this layer. However, the size of the structural features is on the order of those found in the PLZT and peaks from CuO_2 or NiO were not seen in xrd scans. These results suggest that the region may be comprised of reacted or poorly crystallized PLZT. Though this layer is present in the as-deposited films, with the exception of a reduced total permittivity, it appears not to strongly influence the frequency dependent electrical properties. As such, structures containing these interface layers may be appropriate for a functional device application in the frequency range investigated. The influence of these interfaces may become more important if applications are geared towards microwave frequencies.

Foil samples were qualitatively tested after deposition to roughly determine handle-ability. In general, the foils could be repeatedly wrapped around 3 cm diameter mandrels without cracking or delamination. This type of resilience is important as it will facilitate handling and storage on rolls. Moreover, it suggests that these structures will survive the potentially aggressive conditions required for lamination into polymer packages.

CONCLUSIONS

A method has been developed which produces high-K capacitors on base-metal foil substrates suitable for embedding into polymer-based printed wiring boards. Depositing the dielectric on e-Ni coated Cu foils allows all high temperature processing steps necessary for structure and property development to be isolated from the temperature sensitive organic-based packages. The high-permittivity layers were produced by chemical solution deposition. The specific starting composition and firing temperatures were chosen such that high-quality material could be achieved despite the reducing N_2 atmospheres used during crystallization anneals. Shadow mask defined capacitors (Ni or Pt metal) typically exhibited permittivities and loss tangents of 240 and ≤ 0.017 in the frequency range between 0.1 and 100 kHz. Dispersion was limited to approximately 1% / decade in this range. Transmission electron microscopy revealed the presence of a ~ 35 nm interface layer between the PLZT and e-Ni substrate. This layer and its effects on film properties is under continued investigation. Even with the existence of this interface region, the electrical properties appear to be appropriate for capacitor applications.

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