PCLT/P(VDF-TrFE) Nanocomposite Pyroelectric Sensors

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***Abstract*—Thin composite films consisting of 12 vol% of nanosized lanthanum and calcium-modified lead titanate (PCLT) powder embedded in a vinylidene fluoride-trifluoroethylene copolymer [P(VDF-TrFE)] matrix were deposited on silicon (Si) substrates to form pyroelectric sensors with three different configurations. The influences of a thermal buffer layer and back etching of the silicon substrate on the current and voltage responsivities of the sensors were investigated theoretically and experimentally. The specific detectivity of the sensors was also calculated from the measured voltage responsivity and noise.**

I. Introduction

Studies on ferroelectric ceramic/polymer composites were initiated in the 1970s, but most of the composites investigated consist of a passive polymer matrix, such as silicone rubber or epoxy [1]–[5]. P(VDF-TrFE) is a ferroelectric copolymer that has attracted special attention in integrated pyroelectric sensor and array applications [6]–[9]. When the VDF content is in the range of 20 to 50 mol % , the copolymer crystallizes in a polar β form when prepared from the melt or from solution. Hence, P(VDF-TrFE) thin films can be deposited on substrates by spin-casting and then poled in situ to yield high pyroelectric activity. Compared with the sintering of ceramic films, fabrication of P(VDF-TrFE) films is a low temperature process that is more compatible with Si technology. By incorporating nanosized ferroelectric ceramic powder in a P(VDF-TrFE) matrix, composite thin films with both phases ferroelectric can be produced. The advantage of these nanocomposites is that the established low-temperature technology for P(VDF-TrFE) can be directly applied to fabricate pyroelectric sensors. The pyroelectric coefficients of the ceramic and copolymer phases have like sign, and the piezoelectric coefficients have opposite sign; therefore, when the two phases are poled in the same direction, the pyroelectric activities of the two phases are reinforced, and their piezoelectric activities are partially cancelled [10], [11], reducing the vibration-induced electrical noise in the sensor. PCLT was reported to have better pyroelectric properties than lead titanate [12]; hence, PCLT-nanosized powder was prepared by a sol-gel process [13] and used in the fabrication of composites.

In this study, thin PCLT/P(VDF-TrFE) nanocomposite sensors with 12% volume PCLT were deposited on Si substrates by the spin-coating method, and the PCLT and P(VDF-TrFE) phases were poled in the same direction to obtain reinforced pyroelectric properties. Because the Si substrate has a high thermal conductivity and heat capacity compared with the thin composite film, it served as a heat sink, thereby reducing the pyroelectric signal amplitude. To improve the performance of the sensor, it is necessary to reduce the heat flow from the pyroelectric layer to the Si substrate, either by inserting a polyimide thermal buffer layer between the pyroelectric layer and the Si substrate or by back etching the Si wafer.

II. PCLT Powder Prepared by the Sol-Gel Technique

To ensure that the composite films are homogeneous, the inclusions should have as small a size as possible. The conventional mixed oxide method cannot be used, as the resulting powder size is too large. Hence, nanosized $[(Pb_{0.88}Ca_{0.04}La_{0.08})Ti_{0.98}O_3]$ powder was prepared by the sol-gel technique using lead acetate trihydrate, lanthanum nitrate, and calcium acetate as the precursors [13]. The size of the powder can be controlled by varying the annealing temperature T_a because the size increases as T_a increases. However, if the size of the powder is lower than a critical value, the ceramic powder will not have good pyroelectric properties. A study of the X-ray diffraction (XRD) patterns of PCLT powder annealed at various temperatures revealed that the (002) and (200) peaks were clearly separated when the powder was annealed at 850°C, indicating that the powder is in a ferroelectric tetragonal phase. Hence, in this work, PCLT powder annealed at 850°C was used. The powder had an average crystallite size of 45 nm as determined by XRD and an average particle size of 80 nm as determined by a particle size analyzer.

III. Fabrication of PCLT/P(VDF-TrFE) Composites

P(VDF-TrFE) 70/30 mol % copolymer [Curie transition temperature (T_{ch}) = 105°C upon heating and T_{cc} = 70°C upon cooling] supplied by Piezotech (St. Louis, France) was used as the matrix. One gram of P(VDF-

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