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Large Pyroelectric Response from Reactively Sputtered Aluminum Nitride Thin Films

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Since the demonstration of high-efficiency group-III nitride (III-N) light emitting diodes (LEDs) in 1995, this class of compounds has found many other applications in areas as diverse as UV transparent windows and piezoelectric transducers. Because of their wurtzite structures the III-N compounds have also been suggested as possible candidates for pyroelectric (PE) sensors. Calculations by Bernardini et al. and Zoroddu et al. have predicted that III-N compounds should have significantly higher piezoelectric constants and piezoelectric coefficients 5-20 times higher than other III-V and II-VI compounds.

Subsequently, Shure et al. calculated that GaN could have a pyroelectric voltage coefficient of $0.7 \times 10^3$ V/m/K; 40% greater than LiTaO$_3$, the best-known high-temperature pyroelectric material. Recently Bykhover and Shalaev reported experimental observations of pyroelectric response in thin films of gallium nitride that were $10^3$ V/m-K. Because AlN has larger piezoelectric coefficients than GaN, it is reasonable to expect, as suggested in Ref. 2 and 7, that the pyroelectric effect might be higher in AlN. There are several immediate and potential advantages of AlN over traditional pyroelectric materials. Reactively sputtered AlN has a lower dielectric constant than current commercial PE materials, and the AlN dielectric constant is relatively temperature insensitive to at least 300°C. The thermal conductivity of AlN is on the order of 100 times higher than traditional PE materials, even at 300°C. Low dielectric constant and high thermal conductivity are important for fast detector array response operation. Although a Curie temperature has not been established for the PE effect in AlN (it has been estimated at >300°C for GaN), the group III-nitrides in general are high decomposition materials ($>1300$ K) and therefore have a potential to perform at elevated temperatures. Aluminum nitride in particular tends to survive at elevated temperatures, even in oxidizing atmospheres, due to the formation of stable aluminum oxide compounds.

### Experimental

In this study we measured the PE voltage response of thin films of AlN produced by dc reactive sputtering of aluminum in a $3 \times 10^{-3}$ Torr ammonia atmosphere. The power density at the target was $\sim 5$ W/cm$^2$. The substrates were 0.1 Ω-cm, n-type, polished silicon wafers with (111) orientation. The substrates were rinsed in hot acetone, methanol, and DI water, etched in electronic grade buffered HF acid, rinsed in DI water, and dried in a zero grade nitrogen stream. Prior to the sputter deposition, the substrates were heated in situ above 200°C and cooled below 50°C while the chamber was at or below $5 \times 10^{-9}$ Torr. From X-ray diffraction (XRD) patterns the AlN films were determined to be highly disordered with a broad peak corresponding to the d-spacing of the (0002) reflection, which is oriented normal to the substrate surface. Neither the XRD patterns nor ESCA profiles of the AlN layer showed any sign of free aluminum, implying that the films were essentially stoichiometric. Hot probe measurements showed the films to be semi-insulating to slightly p-type with typical through-film resistance of 25 MΩ/μm cm of area. The thickness of films varied from 540 to 2500 Å ± 50 Å controlled by sputtering time. Subsequent to the AlN deposition, a 100-200 Å layer of NiCr was applied, by radio-frequency (RF) magnetron sputtering in argon, to act as both a contact to the AlN and to increase absorbance at IR wavelengths. The n-type silicon substrate was used as the back contact. To measure the PE response, a broadband IR source was focused onto the specimen after passing through a vane chopper. An undoped silicon wafer, etched and polished on both sides, was interposed between the source and the specimen to remove any light of frequency above the band gap of silicon and, thereby, suppress photovoltaic responses associated with substrate absorption.

### Results and Discussion

The voltage response to the chopped IR source is shown in Fig. 1 for one of the specimens. As expected for a pyroelectric material, the AlN film responded to the time rate of change of temperature (d$T$/dt) rather than to the absolute value of temperature difference per sec. A first estimate of response time can be obtained from the exponential decay part of the trace. The relaxation after the initial rise was fitted to an exponential as shown in Fig. 2, from which a 1/e response time of 0.013 s is calculated. By assuming a rise in temperature linearly proportional to the rate of energy input and an exponential fall in temperature proportional to the thermal conductivity of the AlN and Si substrate, then the time to reach the maximum rate of temperature change is 0.011 s, which is close to the 0.0067 s to reach the maximum output voltage. The relationship used to determine $P_V$ is (see, for example, Ref. 8, p. 94)

$$\frac{\Delta V}{\Delta t} = P_V \frac{\Delta T}{\Delta t}$$

where $V$ is the measured voltage, $T$ (K) is the calculated temperature, $t$ (s) is the time, and $h$ is the layer thickness; 600 Å for this specimen.

Both $\Delta V/\Delta t$ and $\Delta T/\Delta t$ are obtained from analysis of the Fig. 2, and a pyroelectric voltage coefficient of $P_V = 0.51-0.69 \times 10^6$ V/m-K was extracted for this particular 600 Å thick AlN layer. The range for $P_V$ depends on how one chooses the time range for calculating $\Delta V/\Delta t$ and $\Delta T/\Delta t$. The thermal responses, shown on the figure, were constructed using material properties values from the literature and a commercial finite difference heat flow calculation program. In Fig. 3 the response to a shuttered IR pulse is shown for a complete cycle. In that figure the peak voltage for the 2500 Å thick specimen is 7.16 mV. There is a residual output, $V_0 = 7.5$ mV, which a 1/e response time of 0.013 s is calculated. By assuming a rise in temperature linearly proportional to the rate of energy input and an exponential fall in temperature proportional to the thermal conductivity of the AlN and Si substrate, then the time to reach the maximum rate of temperature change is 0.011 s, which is close to the 0.0067 s to reach the maximum output voltage. The relationship used to determine $P_V$ is (see, for example, Ref. 8, p. 94)

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during the illuminated part of the cycle which is due to the finite continuous heat flux through the film because of the difference in absolute temperature of its two sides.8

In summary, AlN appears to have a PE voltage response comparable to values found for materials used for commercial detectors8 and greater than that thus far reported for GaN. The crystal symmetry of both AlN and GaN, however, are quite high and so such large PE values are not expected for these compounds. Indeed, Fuflyigin et al.15 measured an AlN PE charge coefficient of $P_Q = 6.8 \pm 0.5 \mu C/(m^2 K)$, which is at least two orders lower than typical for commercial PE materials. Assuming a relative dielectric constant for AlN of $\kappa = 8.5$,10 the $P_Q$ above converts to a PE voltage coefficient of $\nu_0 = 0.008 - 0.01 \times 10^6 \text{V/m-K}$, a factor of 50 lower than we calculate from our measurements. This suggests that there may be other factors such as surface oxidation, deposition related strain, unintentional incorporation of impurities, etc. that might be ultimately responsible for the measured effects. Several groups have calculated the importance of strain doping in the performance of III-N compounds.16-22 Oxygen, for instance, is known to be present in these specimens, at least at the two surfaces of the AlN layer. Additional experiments are under way to evaluate this possibility and to maximize the PE effect in thin layers of AlN.

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