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Letters to the Editor

EVIDENCE FOR PYROELECTRICITY IN Al—SiO_2—Si STRUCTURES

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ДАННЫЕ О ПИРОЕЛЕКТРИЧЕСТВЕ В СТРУКТУРАХ Al—SiO_2—Si

When attempting to analyse thermal current spectra of Al—SiO_2—Si (MOS) structures at the temperature region of 90 K—400 K, we have detected spontaneous currents generated by the virgin (nonpolarized) MOS structures in the course of heating with a zero applied bias. For a variety of the structures the sign of the current flowing through the current meter connected in parallel with the MOS was always such that the gate electrode charged negatively during heating. By contrast, the current has been found to reverse its polarity upon the cooling of the structure, dropping to zero at a constant temperature. The behaviour is illustrated in Fig. 1. The current loop in the figure is not symmetrical around the temperature axis, since the cooling rate employed is nonuniform. Nevertheless, the loop is fully reversible when the thermal cycles are repeated. Thus, the observed effect, not reported previously for MOS structures, possesses all the features required for the reversible pyroelectric effect. Our observation is restricted, of course, to the thermally grown SiO_2 layers on the n-type Si substrates of 10 Ωcm resistivity. A related study on MOS structures with SiO_2 gate oxides prepared by another deposition method is being in progress.

The current flowing during the uniform heating at the rate $v = dT/dt = 0.12\ Ks^{-1}$ enables one to calculate the respective pyroelectric coefficient p defined by the simple relation

$$p = \frac{j}{v}, \tag{1}$$

where j stands for the current density. With a set of samples pyroelectric coefficients ranging from 3.5×10^{-12} to 6.0×10^{-12} C/cm^2 K have been found.

Next, we will discuss possible mechanisms potentially leading to the reversible pyroelectricity in the MOS structures. The discussion will be confined to three main classes of pyroelectricity in solids: i) primary pyroelectricity connected with a temperature dependent spontaneous polarization; ii) secondary pyroelectricity due to piezoelectricity; iii) pseudopyroelectricity related with fixed charges embedded in the dielectric.

As to item i), the thermal SiO_2 layers on Si are widely treated as disordered with a small amount of crystallites formed at some nucleation centres. Adopting this statement, we exclude at this moment the possibility that some native ferroelectric phase would be contained in the thermal SiO_2. A more detailed speculation on the idea of a similarity between the thermal SiO_2 and ferroelectric glass ceramics pyroelectric behaviour is beyond the scope of the present paper [1, 2].

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Our attempt to explain the pyroelectricity in MOS structures as a secondary pyroelectric effect coupled with piezoelectricity of the SiO_2 film is based on the unique experimental work reported by Misawa et al. [3]. The authors were able to prove both electrostriction and piezoelectricity in thermally grown and sputtered SiO_2 films. Now, let us estimate the cotribution of piezoelectricity to the pyroelectric effect. The formula for the secondary pyroelectric effect is [4]

$$p_s = \frac{\alpha d}{s} \tag{2}$$

where α is the coefficient of thermal expansion, d is the piezoelectric modulus and s is the compliance. Under the assumptions $d \simeq d_{31}$ and $s \simeq s_{11} = 1/E$, taking the values $d_{31} = 9 \times 10^{-14}$ cm/V [3], $E = 6.6 \times 10^{11}$ dyn/cm^2 [5], $\alpha = 10^{-7}$ K^{-1} [6], we obtained $p_s = 6.5 \times 10^{-16}$ C/cm^2 K. The latter value is four orders of magnitude lower than the one obtained from the measurement of the pyroelectric current. From this point of view the interpretation of the pyroelectric effect as a secondary one seems incorrect. Strictly speaking, when applying equation (2) to our case, we have assumed expansion of the film only in the direction of its thickness. The real situation is such that the film is partially clamped to the substrate. Taking into consideration also the expansion of the film in the basal plane, Zook and Liu [7] derived an additional contribution to the total p of the form

$$p_s' = \frac{-2d_{31}(\alpha - \alpha_s)}{s_{11} + s_{12}}, \tag{3}$$

α_s being related to the substrate and $s_{12} = -\nu s_{11}$. For the evaluation we consider $\alpha_s \simeq 10^{-6}$ K^{-1} [8] and the Poisson ratio of the SiO_2 film $\nu \simeq 0.18$. The coefficient p_s' is then the order of 10^{-15} C/cm^{2}K, so the effect of clamping the film appears to be still insufficient for achieving an agreement between the experiment and the theory. In addition, both α and α_s are strongly temperature dependent, implying the same tendency for p, again in contradiction with the experiment — see Fig. 1.

The occurence of a pyroelectric effect related to charges embedded in a dielectric which is not homogenous was treated independently by Salomon et al. [9] as well as by Wada and Hayakawa [10]. All the authors considered gradients in both the linear coefficient of thermal expansion α and permittivity ε in the thickness direction of the dielectric containing a frozen space charge. It is convenient to analyse the contribution of each type of gradient separately. In the case of the dielectric constant being invariant to space and temperature, the pyroelectric coefficient is adequately described by the relation [9]

$$p = -\int_0^{L_0} \frac{\alpha(x)}{L_0} \left(\int_0^x \varrho^0(x)\,dx - \frac{1}{L_0} \int_0^{L_0} \int_0^x \varrho^0(x'')\,dx''\,dx \right) dx, \tag{4}$$

where $\alpha(x) = \alpha_0(1 + \alpha^* \xi x / L_0)$. To obtain an approximate value of $\varrho^0(x)$, we assume a uniform charge density ϱ^0. Then, taking $\alpha^* \xi = 0.1$, $\alpha_0 = 10^{-7}$ K^{-1}, $L_0 = 2 \times 10^{-5}$ cm, the charge density ϱ^0 on the order of 10^{21} cm^{-3} is required to explain p found experimentally. This density is unreasonably high. Another argument against the "gradient in α" approach is the temperature dependence of α already mentioned above. We will, therefore, judge the chance of a gradient in ε in interpreting the pyroelectricity in the SiO_2 films. The approximate expression for p is of the form ($\alpha^* = 0$) [9]

$$p = -\xi L_0 \left(\frac{a_0 \varepsilon^*}{\varepsilon_0^0} - \frac{a_0 \alpha^*}{\varepsilon_0^0} \right) \sum_{n=0} C_n g_n, \tag{5}$$

where $g_n = [2(n+2)(n+3)]^{-1}$. The symbols ε^* and α^* denote the gradients in both the temperature-independent and the temperature-dependent part of permittivity. The gradients are defined in the same way as α^* defined above. We assume again the case of a spatially constant charge density ($n = 0$). Choosing the values $a_0/\varepsilon_0^0 = 3 \times 10^{-5}$ K^{-1}, $\varepsilon^* - \alpha^* = 0.2$, $\xi = 1$, $L_0 = 2 \times 10^{-5}$ cm, the charge density

of 10^{18} cm^{-3} is necessary to fulfil (5). The density of native charged centres in SiO_2 on the order of 10^{18} cm^{-3} might be real with regard to the theoretical prediction of Mott et al. [11]. The latter value might correspond to the concentration of some unidentified impurity ions as well. Further effort is required to settle this point.

Finally, a valuable information can be extracted from the work published by Hickmott [12], which work is somewhat relevant to the present study. In the course of his own measurements of thermally stimulated ionic conductivity in SiO_2 an almost temperature independent current component was registered above ambient temperature. Hickmott called it "background current" without further

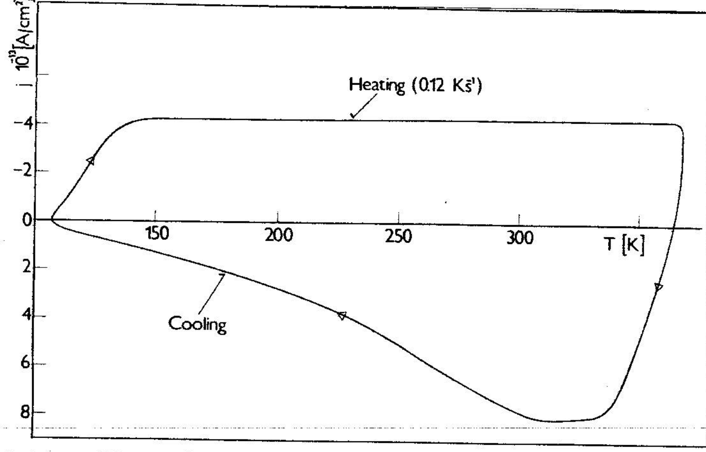

Fig. 1. A reversible pyroelectric current loop characteristic of an Al—SiO_2—Si(n) structure.

specification. We suggest that we deal with pyroelectric currents in the case of Hickmott's measurements, too. A precise quantitative analysis of the latter measurements is complicated by the hyperbolic rate scheme utilized by Hickmott [12]. From a linear approximation of the heating rate in [12] an equivalent heating rate of ~ 1 Ks^{-1} follows. Now we are able to calculate the pyroelectric coefficient using (1) and the current density of $\sim 2 \times 10^{-9}$ A/cm^2. As a result the value $p \sim 2 \times 10^{-9}$ C/cm^2 K is obtained. This value is by three orders of magnitude greater than that found in the present study. This significant difference is evidently a result of the polarization and biasing conditions employed by Hickmott [12]. An important point to make is that such „poled" MOS devices exhibit a pyroelectric coefficient comparable to that of polyvinylidene fluoride [10], which polymer is suitable for applications as a detector for infrared radiation.

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