L. Kasprzak
A. Hornung

Polarization and Depolarization in PSG Films

Abstract: The temperature dependence of the polarization in thin phosphosilicate glass (PSG) films is characterized by an activation energy $\Delta H = (0.39 + 0.039Et)$ eV, whereas the decay mechanism has an activation energy of 0.5eV. The flatband voltage shift due to PSG polarization was linear with applied fields as large as $5.5 \times 10^6 \text{V} \cdot \text{cm}^{-1}$. The effective time constants for the polarization and depolarization are distinctly different. Polarization occurs an order of magnitude faster than depolarization. A physical model has been postulated to explain the observed effects.

Introduction

Thin phosphosilicate glass (PSG) films are used extensively throughout the semiconductor industry as Na^+ ion barriors. PSG films containing approximately four mole-percent P_2O_5 and of the order of 125Å thick have been found to be very effective in blocking Na^+ ion concentrations as high as $10^{12} \cdot \text{cm}^{-2}$ [1]. The major disadvantage in using PSG films in field effect transistor (FET) devices for threshold voltage stabilization is that these films polarize and therefore contribute to the shift in threshold voltage. This polarization instability has been studied and reported in the literature [1, 2, 3]. The demand for increased performance of integrated circuits and for special applications requiring precise threshold voltage control have made it imperative to reexamine some aspects of PSG polarization in more detail.

When a voltage is applied across an MGOS (metal–PSG–oxide–silicon) sandwich, polarization of the PSG layer occurs. The degree of polarization depends upon the value of applied voltage and the duration of the application. In general, the dielectric constant of such PSG layer is

$$\varepsilon = \varepsilon' + \chi, \tag{1}$$

where ε' is the dielectric constant at high frequency and χ is the polarizability of the PSG.

The polarization in MGOS FET devices manifests itself as a change in threshold voltage ΔV_t. It can be shown that the polarization shift saturates according to the following relation [2]:

$$\Delta V_t = -\frac{\varepsilon_0 t_g \chi V_p}{\varepsilon_g[(\varepsilon_g + \chi)\, t_0 + \varepsilon_0 t_g]}, \tag{2}$$

where

ε_0 = dielectric constant of the oxide,
ε_g = dielectric constant of PSG,
t_g = thickness of PSG,
t_0 = thickness of oxide, and
V_p = applied polarizing voltage.

For structures where $t_g \ll t_0$, Eq. (2) reduces to

$$\Delta V_t = -\frac{\chi t_g V_p}{\varepsilon_g t_0}. \tag{3}$$

If χ becomes very large Eq. (2) reduces to

$$\Delta V_t = -\frac{\varepsilon_0 t_g V_p}{\varepsilon_g t_0}. \tag{4}$$

In general, two mechanisms for PSG polarization have been reported. The first mechanism, attributed to a dipolar rearrangement, occurs relatively fast and saturates according to Eq. (2). The second mechanism occurs at high temperature, i.e., >200°C, and has been called the slow component. This mechanism has been attributed to a slow charge drift over many atomic distances until space charges have been built up at the metal-glass and glass-oxide interfaces [2]. In this case, the polarizability χ becomes very large and Eq. (4) predicts the saturation shift. Fortunately, for most applications the slow polarization component is negligible. This study therefore only concerns itself with the so-called *fast* polarization.

Recently, during a study of the reliability of complementary FETs with MGOOS (metal–PSG–pyrolytic SiO_2–thermally grown SiO_2–silicon) gate structures, some difficulty was experienced in measuring the threshold voltage shifts ΔV_t after bias temperature stressing. The difficulty arose because a computer-interfaced tester was being used, which took approximately one hour to

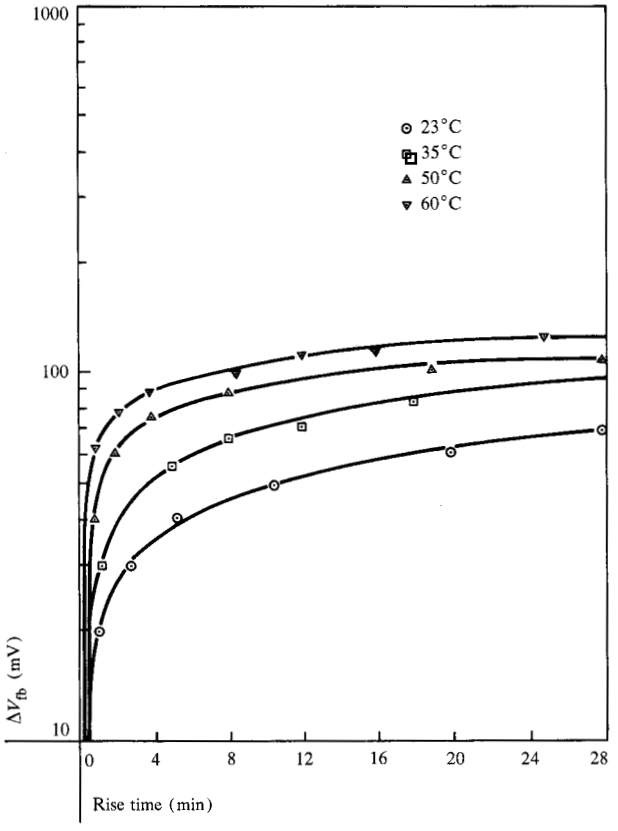


Figure 1 Flatband voltage shift ΔV_{fb} vs time for PSG polarization buildup at various temperatures for n capacitors polarized at −15 V.

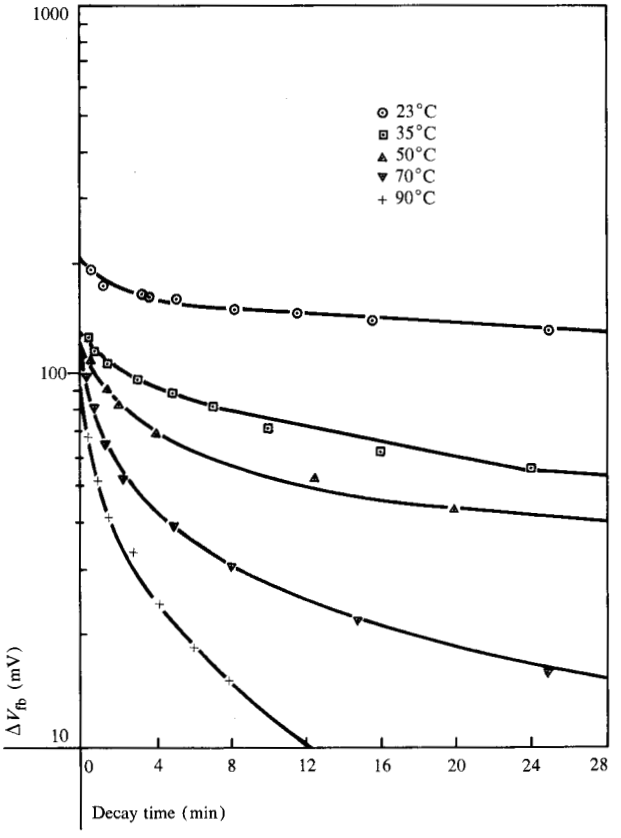


Figure 2 Flatband voltage shift ΔV_{fb} vs time for PSG polarization decay at various temperatures for n capacitors polarized at −15 V.

measure all the devices. The actual readout time, after removal of the voltage bias, was found to be critical and actually determined the shift that would be measured, since the shift due to polarization begins to decay immediately after the removal of the bias. As a result an investigation of the buildup and decay of PSG fast polarization was initiated. From the outset it became clear that the buildup and decay time constants were different. Also, the degree of thermal activation of the buildup seemed different from that of the decay. This paper examines

- the buildup time constant and its thermal activation,
- the decay time constant and its thermal activation, and
- the temperature and voltage dependences of PSG polarization.

Experimental procedure and sample description

The samples used for this experiment were all essentially MGOOS structures. Both n and p channel FET devices and capacitors were employed. The capacitors were 0.5mm circular aluminum electrodes deposited on top of the PSG. The mole percent and thickness of PSG as well as the oxide thickness are listed in Table 1.

All values in the table are averages calculated from about ten wafers per process run; N_D and N_A are, respectively, the donor and acceptor silicon doping levels. PSG thicknesses and mole percents were determined by standard etching techniques.

The polarization effects on FET devices were studied by performing threshold voltage measurements with an automatic tester as a function of time. Approximately

Table 1 Sample description.

Process run	t_{ox}(Å)	t_g(Å)	P_2O_5 (mole %)	$N_D(10^{16}\,cm^{-3})$	$N_A(10^{16}\,cm^{-3})$
Capacitor	386	136	4.0	1	8
FET-1	416	104	1.5	1	8
FET-2	356	126	3.1	1	8
FET-3	419	136	3.9	1	8

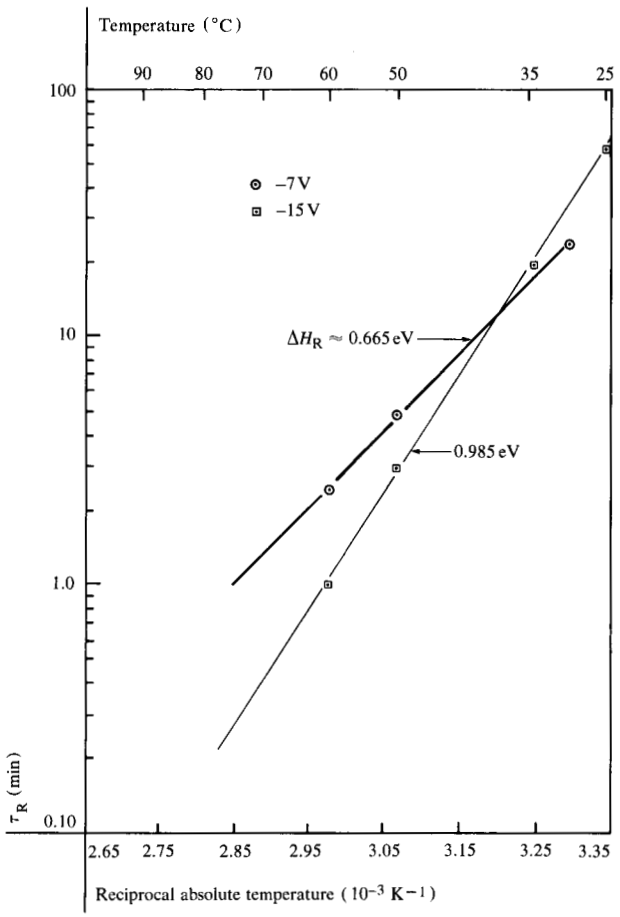


Figure 3 PSG polarization buildup time constant τ_R vs reciprocal absolute temperature for n capacitors.

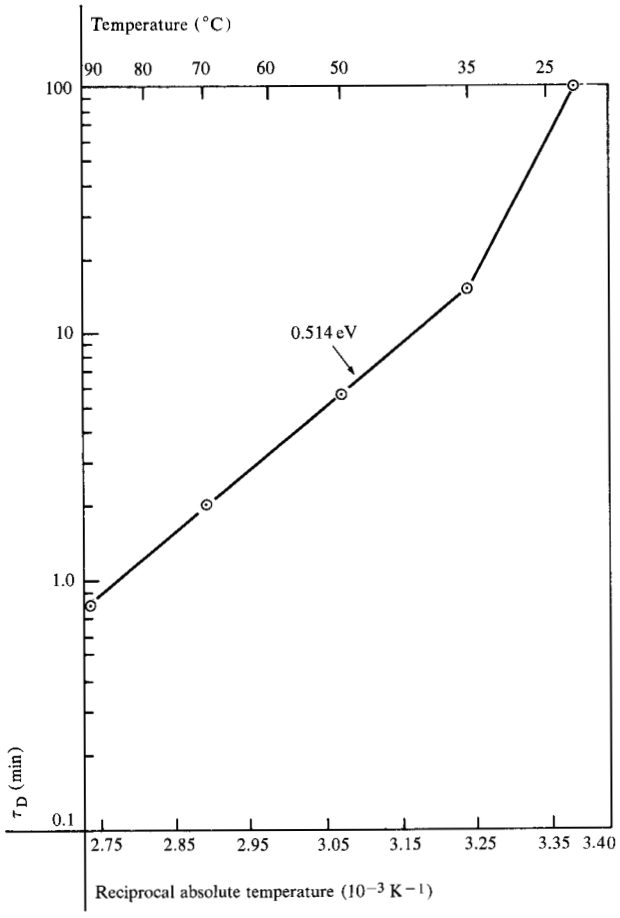


Figure 4 PSG polarization decay time constant τ_D vs reciprocal absolute temperature for n capacitors polarized at −15 V.

40 capacitors were measured by the MOS capacitance voltage (C-V) method. The technique consisted of essentially applying a polarizing voltage to a sample mounted in an oven and then performing a rapid C-V trace at regular intervals of time. The voltage sweep was restricted to about ± 500mV around the flatband voltage. The accuracy of the measurements was within ± 10mV. Extreme care was taken to minimize the effect of read-out time on both buildup and decay time constants. Specifically, on buildup, the measurement time was kept constant at 5s so that it would be a negligible part of the total time of buildup. On decay measurements, the clock was started at the time of the removal of the polarizing voltage.

Before performing decay measurements on the FET devices, samples were stressed for two to three days. The substrate, source and drain were grounded and a bias voltage was applied to the gate. The devices were stressed at 85 °C and 165 °C at 8.5V and 15V. After stressing, the devices were cooled under bias to 23 °C. A total of 162 devices were studied. These devices were selected from the three process runs shown in Table 1.

Experimental results

Typical PSG polarization buildup and decay curves for capacitors are shown in Figs. 1 and 2, respectively. The polarizing voltage was −15V. The polarization buildup progresses an order of magnitude faster than the decay, a phenomenon that, to our knowledge, has not been reported previously. It was also observed from the plots that the buildup and decay mechanisms are not exponential and therefore cannot be characterized by a single time constant. To fit these curves, a broad distribution of time constants is required, such as

$$\Delta V_{fb}(t) = \Delta V_{fbSAT} \sum_{i=0}^{N} k_i \exp(-t/\tau_i), \quad (5)$$

where k_i is a proportionality constant, N is empirically chosen to fit the curve, and $t = t_0 + t_g$.

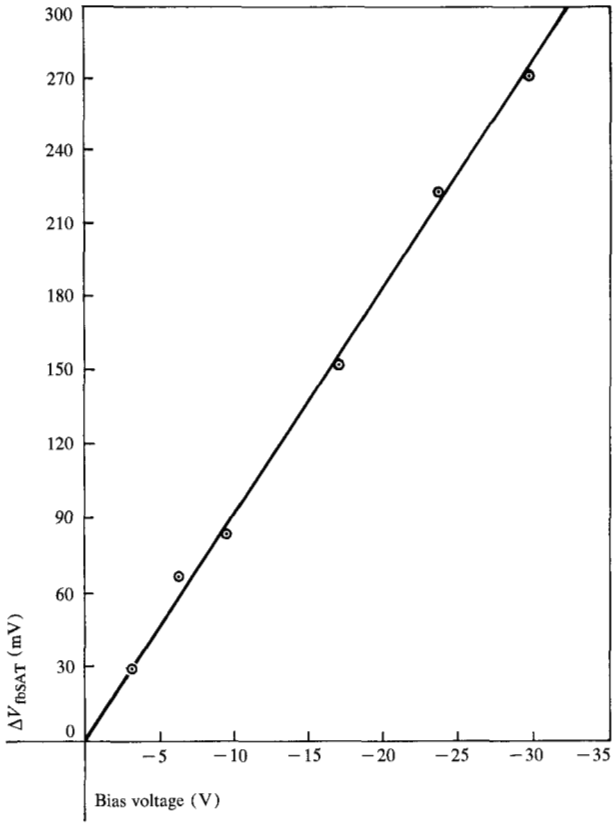


Figure 5 PSG polarization saturation ΔV_{fbSAT} vs bias voltage at 50 °C for n capacitors with 386 A of SiO_2 and 136 Å of four mole-percent P_2O_5.

The polarization rate has a strong temperature dependence. The effective time constant τ_R is defined as the time required to reach 50 percent of the saturation value. These effective time constants are plotted against reciprocal absolute temperature in Fig. 3 for applied voltages of −7V and −15V. The slopes yielded activation energies of 0.67eV at −7V and 0.99eV at −15V bias. These were in excellent agreement with the activation energies reported by Snow and Deal, ≈1eV [2], and by Eldridge, Laibowitz and Balk, ≈0.98 ± 0.05eV [3]. The decay mechanism is again a strong function of temperature (Fig. 4). The time required to decay to 50 percent of the saturation value is defined as the effective decay time constant τ_D. An activation energy of ≈0.5eV was calculated.

The ΔV_{fbSAT} as a function of bias voltage was plotted in Fig. 5. As expected, ΔV_{fbSAT} was proportional to the polarizing voltage. The slope was 9mV per volt of bias voltage at 50 °C. This straight-line relationship holds at least up to −30V bias.

The polarization decay curve for typical discrete FET devices was plotted in Fig. 6. The striking feature of this curve is that the decay is proportional to log t between 5 and 500 minutes. This is not to say that the decay curves themselves or the decay constant τ_D are different from the capacitor structures. Examination of Figs. 7 and 8 reveals that the decay is similar to that observed for the capacitors. Further, the decay constant for the complementary devices at 23 °C is roughly 1.5 h which compares quite favorably with the decay constant of ≈100 min at 23 °C for the capacitor structures (Fig. 4).

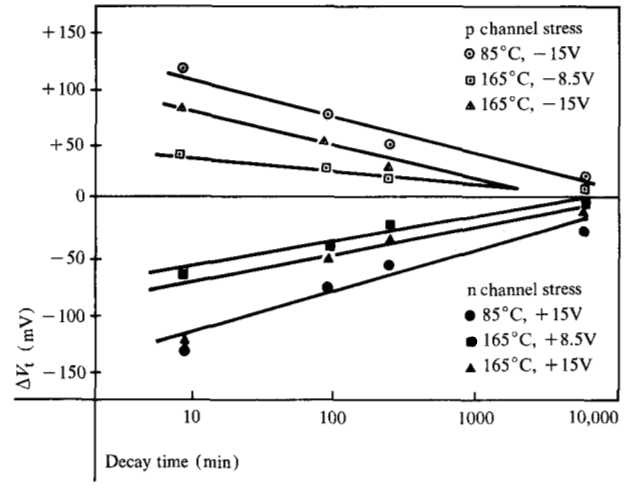


Figure 6 FET polarization ΔV_t decay vs time at 23 °C for typical n and p channel devices.

Finally, it should be noted that the value of ΔV_{tSAT} for the FET structures is proportional to the mole percent P_2O_5, as expected:

	Mole %	$\Delta V_{tSAT}(mV)$
FET-1	1.5	125-150
FET-2	3.1	200-250
FET-3	3.9	175-200

The agreement is well within normal process variability.

Discussion

That the polarization cannot be characterized by a single time constant is shown by the nonlinearity of Figs. 1 and 2. The family of curves can be characterized by an effective time constant τ that is related to temperature by

$$\tau \propto \exp(\Delta H/kT), \tag{6}$$

where ΔH is the activation energy, k the Boltzmann constant, and T the absolute temperature.

The polarization buildup is characterized by an activation energy which is a function of the applied polarizing field. The activation energy is therefore

$$\Delta H_R = \Delta H_0 + \alpha E, \tag{7}$$

where $\Delta H_0 = 0.39\text{eV}$, $\alpha = 0.039e$, and E is the applied field.

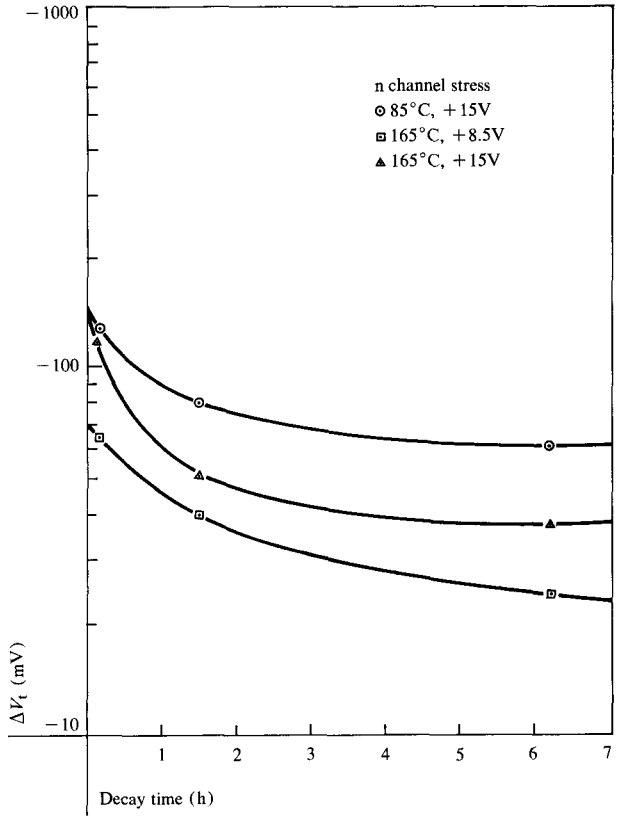


Figure 7 FET polarization ΔV_t decay vs time at 23 °C for typical n channel devices.

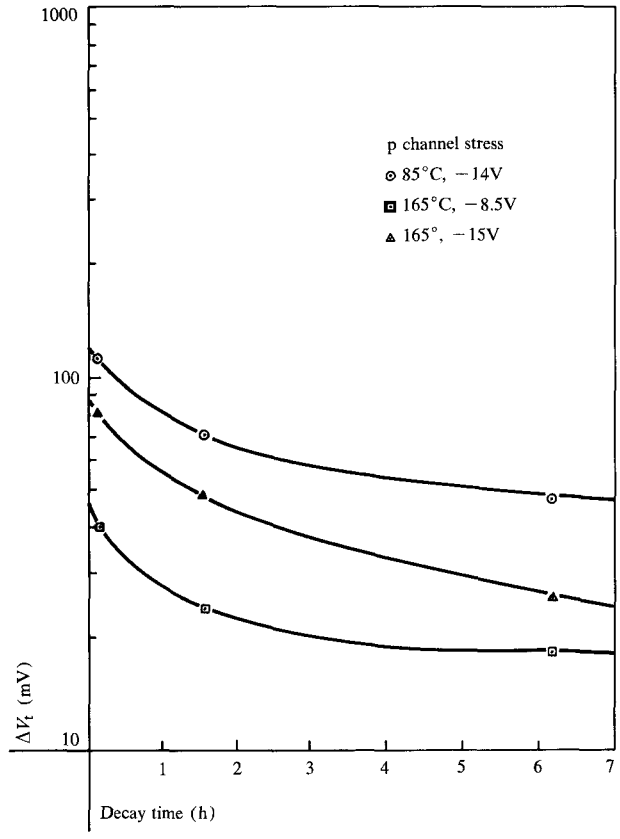


Figure 8 FET polarization ΔV_t decay vs time at 23 °C for typical p channel devices.

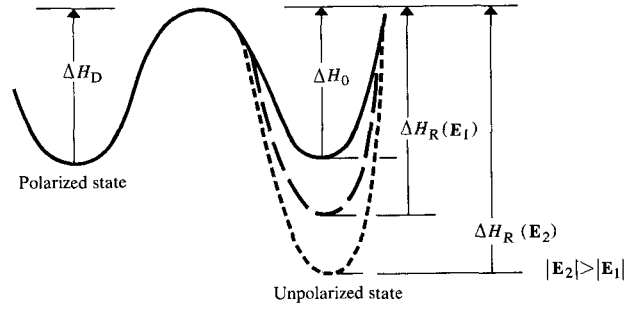
The polarization decay is characterized by an activation energy of ≈0.5eV. No comparison to previous work is possible since decay constants have not been published previously. The thermal activation of the decay is not characterized by a single decay mechanism. This was evidenced by the change in slope of τ_D vs reciprocal absolute temperature (Fig. 4) between 35 °C and 23 °C. It should be noted that there is some indication in Fig. 4 that the activation energy is ≈1eV below 35 °C. This may indicate a change in the depolarization mechanism below room temperature.

Applying equation (2) to our results yields a polarizability $\chi_p \approx 0.22$. Snow and Deal [2] reported $\chi_p \approx 0.75$ for 15.5 mole percent P_2O_5.

Thus far no mention of Na^+ ion contamination has been made. The reason is that the samples used in this experiment had very little contamination, as evidenced by the symmetry of the n and p channel decay curves (Fig 6). For the capacitor samples, contamination levels were of the order to $10^{10}\ e \cdot cm^{-2}$. Further, only negative bias voltages were used on these samples to minimize any possible effect of contamination.

Returning to the activation energy of build-up and decay, one can postulate a model of the observed activation energy after the known energy dependence of a dipole **P** in an electric field, $E_p = -\mathbf{E} \cdot \mathbf{P}$. This well known formula indicates that the dipole gives up energy proportional to the applied field upon polarization. Hence, the apparent activation energy should be field dependent because the final energy level of a polarized molecule of P_2O_5 in SiO_2 depends upon the applied field. This field enhancement of the barrier is just the opposite to the barrier lowering found for ionic diffusion in an applied field. So, for polarization buildup one can model the barrier as shown in Fig. 9, where the apparent activation

Figure 9 Proposed model for the increase of buildup activation energy ΔH_R with applied field E; $\Delta H_1 = 0.665$eV for $E_1 = 1.28 \times 10^6$ V · cm^{-1}; $\Delta H_2 = 0.985$eV for $E_2 = 2.70 \times 10^6$ V · cm^{-1}; $\Delta H_0 \approx 0.50$eV.



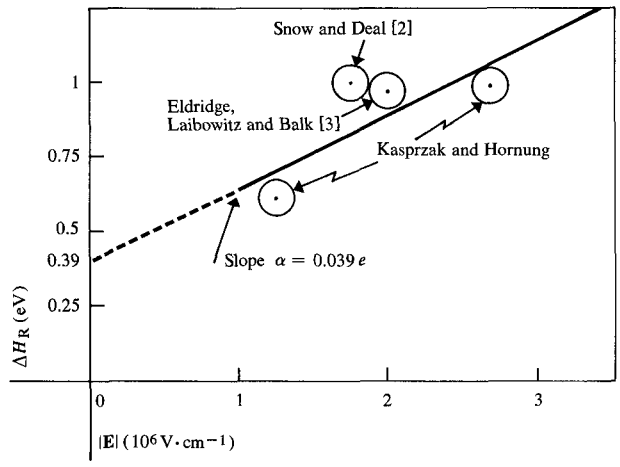


Figure 10 Buildup activation energy ΔH_R vs applied field E.

energy increases with applied field. This effect has not previously been reported. However, activation energies for polarization buildup [2, 3] do fit our field-enhanced model, as shown in Fig. 10.

The activation energy for decay should likewise be field dependent, since the polarized molecule must decay from an energy level which depends upon the applied field (**E**) that was present when the molecules became polarized. All decay curves were measured on samples polarized at the same field; hence this effect was not observed. Further, τ_D is small at 70 °C and 90 °C and therefore the error is potentially significant and could mask this effect.

Extreme care must be exercised in determining shifts in V_t due to polarization phenomena. At 23 °C an error of 37 percent in ΔV_t due to polarization can be introduced by a 10 minute delay in the measurement of V_t after bias removal. At higher temperatures depolarization can introduce even greater errors. For example, at 90 °C, a 10 minute delay will result in an 87 percent error.

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The authors are located at the IBM System Products Division Laboratory, East Fishkill (Hopewell Junction), New York 12533.