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STUDY OF THE PHOTOVOLTAIC EFFECT IN THIN FILM BARIUM TITANATE

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Entitled

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Abstract

A radio frequency sputtering technique developed at the University of New Mexico is currently being used to deposit ferroelectric barium titanate films on silicon and quartz. The photoelectric effect is being observed in structures consisting of metal-deposited barium titanate film-silicon. Film properties are being measured and correlated with the photoelectric effect characteristics of the films.

1. Introduction

Barium titanate films are being r.f. sputtered on silicon substrates. The process is being refined to improve the ferroelectric characteristics of the films. The present films exhibit a relatively high photovoltaic effect. Initial tests appear to indicate that there is a barrier or p-n junction effect in addition to the photovoltaic effect related to the polarization effect in the ferroelectric film. Part of the photovoltaic effect is switchable as a function of the polarization of the film. We are in the process of analyzing the phenomenon.

2.1 Sample Preparations

Thin films of $BaTiO_3$ were sputtered using a commercial r.f. diode sputtering system (cvc Model AST-300) with lower driven electrode holding a 5-in. diameter 99.99 percent pure $BaTiO_3$

target. Sputtering occurred upwards onto a 7-in. diameter grounded electrode holding a 2-1/2-in. square substrate heater, mask and substrate. The bias voltage in the plasma with respect to the positive ions was monitored. Slow deposition rates (5 to 7 Å/min), corresponding to a target bias of -400 to -430 V at various substrate temperatures were investigated.

A standard high vacuum pumping system was employed consisting of a 6 in. diameter oil diffusion pump with a freon trap and a rotary vane foreline pump with a molecular sieve trap. The ultimate system pressure was about 6×10^{-8} torr. Before the sputtering session, ultra-high purity oxygen and argon were bled into the system for a typical 5 to 10 percent O_2 in an argon-oxygen mixture. After the desired percent mixture had been obtained the high vacuum valve was choked down to get the desired sputtering pressure in the bell jar, this was in the 19 to 20 μm range. During every sputtering session, the $BaTiO_3$ target was sputtered clean for one hour before opening the shutter to deposit onto the silicon substrate. A few samples after the deposition were heat treated at 900°C in one atmosphere of ultra-high purity oxygen for a few minutes.

Single crystal silicon wafers doped with phosphorus (n-type) and cleaved parallel to the (100) plane were used as substrate material. The resistivity was 5 Ω-cm which corresponded to 1×10^{15} atoms/cm^3 doping level. Before the film deposition, the wafers were thoroughly cleaned and etched in a buffer Hf solution to strip off the SiO_2 layer. Then the wafers were mounted on the substrate heater assembly and the assembly then mounted in the vacuum system which was pumped down to 10^{-8} torr range. To test the ferroelectric properties of $BaTiO_3$ films, a metal-insulator-semiconductor (MIS) structure was formed. Silicon wafer was used as the lower electrode and a layer of high purity (99.999 percent) gold was thermally evaporated on the back of each wafer. Then the wafer was heat treated to 400°C for five minutes to ensure eutectic bonding between the silicon and gold. This way we have a good ohmic contact between the probe and the wafer. The upper electrode was formed by thermal evaporation of high purity (99.99 percent) chromium pellets. In a few cases indium oxide (In_2O_3) was also tried as the upper electrode.

2.2 Electrical Measurements

The open circuit photovoltage for the MIS sandwich structure was measured using a victoreen electrometer (Model 475B) which had an input impedance greater than 10^{12} Ω. Illumination was from a high-intensity monochromatic ultraviolet source of 366 nm, roughly that of the band-gap energy. Intensity was calibrated with the help of a blakray ultraviolet intensity meter placed in the path of the light flux with the wafer removed. The photocurrent and photovoltage measurements were made at thermal equilibrium. For poling the wafers, a field of about 2.5 x 10^6 V/cm or less for a maximum of 5 minutes was applied.

3. Results and Discussion

A wafer which has never been illuminated, shows no photovoltage. The photovoltage produced by illumination eventually vanishes when the illumination is removed. Further, the photo-emf developed is negative at the top electrode.

The photocurrent increases with light intensity, whereas the photo-emf was a function of intensity at low intensities, but saturating at higher levels. The relation between photo-emf and intensity is shown in Figure 1. The results which are for a particular wafer is typical of others. As observed, the unpoled wafers gave lower photovoltage as compared to the poled ones. As the poling voltage was increased the photovoltage increased till the remanent polarization saturated. Once the wafer was poled, it remained in that state. Annealing in oxygen atmosphere, however, reduced the photovoltage output.

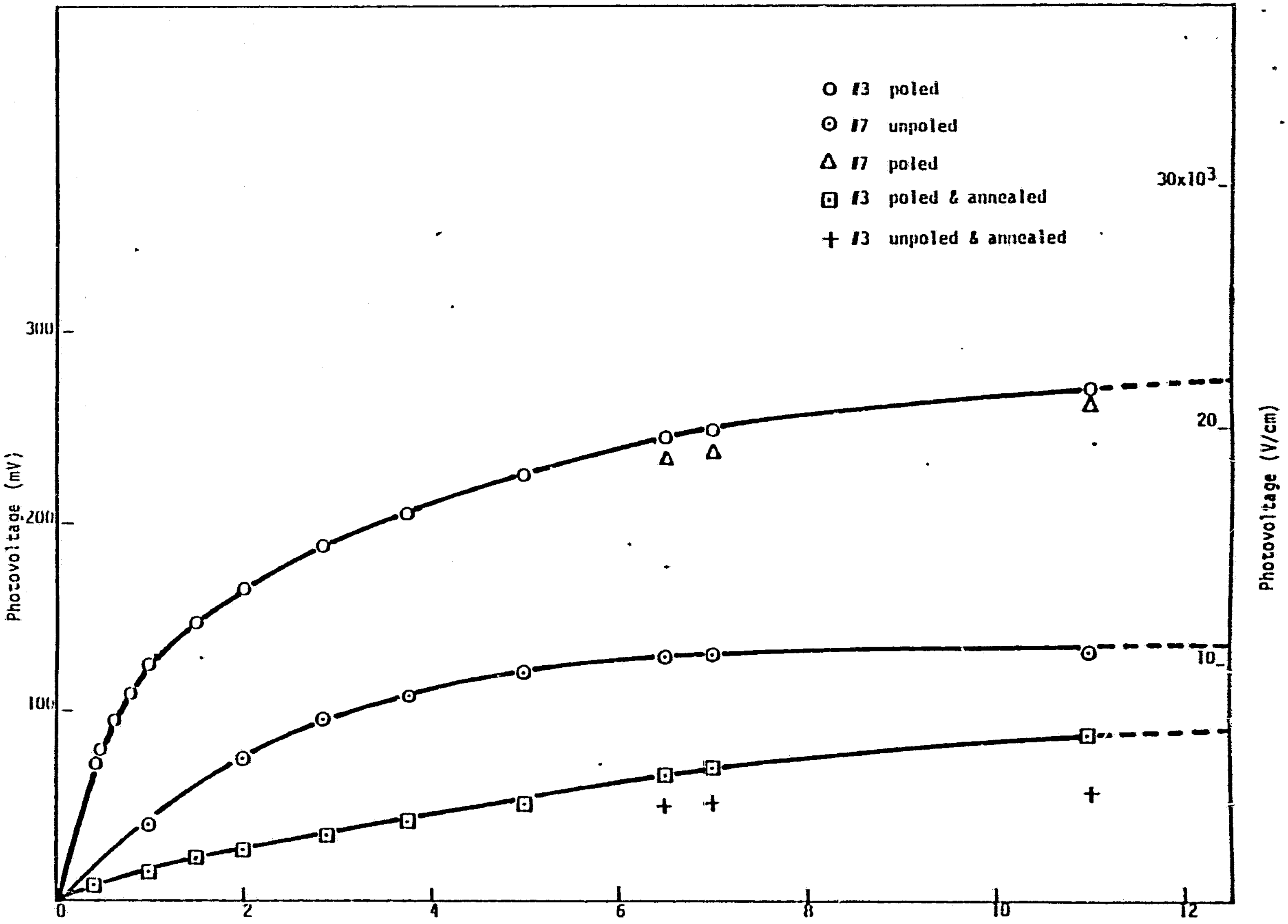

Figure 1. Intensity (mw/cm^2).

In general, to obtain crystalline films of $BaTiO_3$ which exhibit better film properties, it is necessary to deposit the films at higher substrate temperature. Upon cooling, however, microcracks generally develop because of mismatch in the thermal expansion coefficient of $BaTiO_3$ ($8 \times 10^{-6}/°C$) and silicon ($2.5 \times 10^{-6}/°C$ at 20°C). This problem is solved by slowly reducing the substrate temperature at a rate of 5 to 6°C/min during the last part of the deposition. For substrate temperature above 200°C when mentioned in this report, this cooling procedure was followed and the final substrate temperature when deposition ended was between 180 to 200°C. Figure 2 illustrates the influence of substrate temperature on the photovoltage output. All the films were prepared under identical conditions of Ar/O_2 mixture, substrate bias voltage and sputtering time. Unpoled wafers, in general, gave a constant photo-emf output at different substrate temperatures where as poled wafers they showed an increase in photo-emf output with increase in substrate temperature. Annealed samples on the other hand gave lower photovoltages and showed a decreasing trend with substrate temperature. Table 1 summarizes the saturated photo-emf results obtained for poled, unpoled and annealed samples at various substrate temperatures. The photovoltage output for the MIS structure with the In_2O_3 as the top electrode is also included in the table. As seen, the photovoltage output is lowered. This is probably due to the nonstoichiometric nature of In_2O_3 contact. It is known that In_2O_3 on thermal evaporation dissociates to lower suboxide and/or In metal, thus resulting in nonstoichiometry.

According to reported literature to obtain reproducibly-consistent ferroelectric $BaTiO_3$ thin films on silicon substrates, it is necessary to deposit the films at substrate temperatures above 500°C. In Table 2, the saturated photo-emf result for $BaTiO_3$ film sputtered at 660°C substrate temperature is summarized. The wafer was polarized in either direction by applying a high voltage (40 V for a maximum of one minute). The photo-emf changes

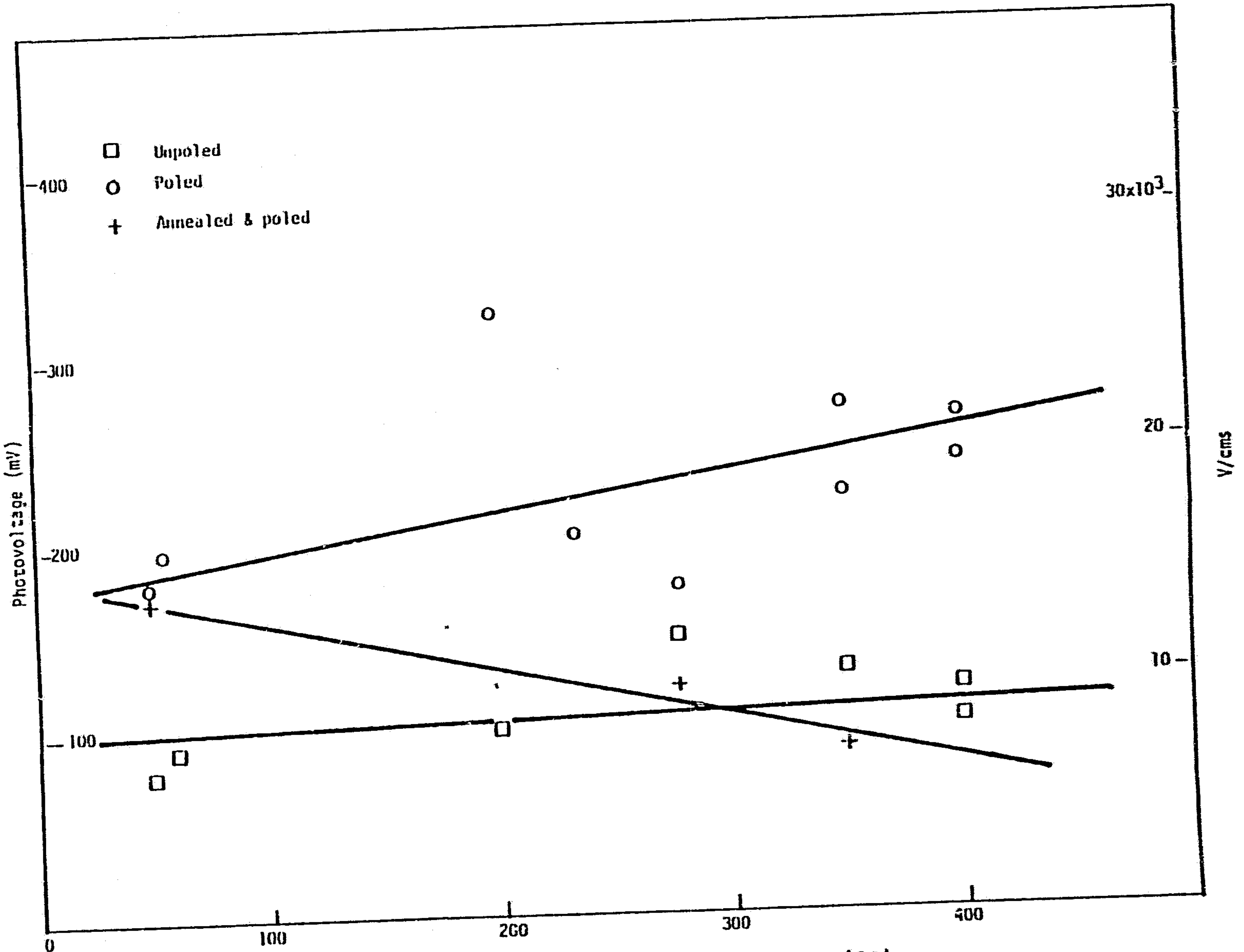

Figure 2. Substrate Temperature (°C).

Table 1

Photovoltaic Output at Room Temperature for Various Deposition Conditions†

No.	Sub-temperature (°C)	Saturated* Poled Photo-emf (mV)	Saturated Unpoled Photo-emf (mV)
4	50	180	80
		175**	-
8	55	195	90
5	201	320	109
1	234	204	-
2	278	175	150
		120**	116
		62***	50
3	349	270	-
		223	130
		90**	62
7	400	265	128
		240	102

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†Values are for polarization in one direction. The photo-emf developed on upper elecrode is negative.

*Illumination wavelength of 366 nm.

**Annealed in O_2 at 900°C for 5 minutes

***Annealed in O_2 at 900°C for 5 minutes and In_2O_3 contact.

Table 2

Summary of Photo-emf Data for $BaTiO_3$ Film Sputtered at 660°C Substrate Temperature in 10 Percent O_2 for Different Switching Cycles. Voltage Applied = 40 V

No. of Cycles	Saturation Photo-emf (mV) (Upper Electrode Poled Positive, 40 V)	Saturation Photo-emf (mV) (Upper Electrode Poled Negative, 40 V)
1	-70	-185
2	-68	-189
3	-88	-190
4	-94	-170
5	-94	-168

for the first few cycles is given. As seen, though the polarity of the photo-emf is the same in the two cases, the magnitude of the photo-emf developed across the electrodes is found to be different. When polarized in the positive direction (i.e., when upper electrode is poled positive) the resultant photo-emf is less as compared to when the wafer is polarized in the negative direction (i.e., the upper electrode is poled negative).

4. Conclusions

The high voltage photovoltaic (24×10^3 V/cms) in thin films of $BaTiO_3$ produced by r.f. sputtering is a new effect and most significant contribution at the moment. At present, the source of switchable emf's is not known, although they appear related to the spontaneous polarization of the material, showing same barrier-like qualities. To obtain good quality pin-hole free films, it has been found necessary to reduce the substrate temperature during the last part of the deposition at a rate of 5 to 6°C/min to a final temperature of about 200°C. Further, the switching ability of the device with internal applied voltage is encouraging from the ferroelectric memory device application point of view. However, improvement in the device characteristics is still needed.