Annual Report

on

STUDY OF THE PHOTOVOLTAIC EFFECT IN THIN FILM BARIUM TITANATE

by

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1. Introduction

This is the first annual report of a research program, "Study of Photovoltaic Effect in Thin Film Barium Titanate," supported by the National Aeronautics and Space Administration under Contract No. NAG-1-95. The object of this research is to synthesize ferroelectric films of barium titanate on silicon and quartz substrates, and to study the photoelectric effect in structure consisting of metal-deposited ferroelectric barium titanate film-silicon (MFS). An anomalous photovoltaic phenomenon is observed in these films—a photovoltage with polarity that depends on the direction of the remanent polarization.

The principal approach used in this program is the deposition of BaTiO$_3$ on silicon and fused quartz substrates by an r.f. sputtering technique developed at the University of New Mexico. We have conducted a series of experiments to study the growth of ferroelectric BaTiO$_3$ films on single-crystal silicon and fused quartz substrates. The ferroelectric character in these films has been found on the basis of evidence from the polarization-electric field (D-E) hysteresis loops, capacitance-voltage (C-V) and capacitance-temperature (C-T) techniques and from x-ray diffraction studies. Initial tests indicate that the anomalous photovoltaic effect appears to be due to a barrier or p-n junction effect in addition to the photovoltaic effect related to the polarization effect in the ferroelectric films. Part of the photovoltage is switchable as a function of polarization of the films. The results on fused quartz are not complete, however, attempts to refine the properties of the films are in progress.

2. Experimental Details

2.1 Sample preparation - Thin films of BaTiO$_3$ were sputtered using a highly modified commercial r.f. diode sputtering system (CVC Model AST-300) with a lower driven electrode holding
a 5-inch diameter 99.99 percent pure BaTiO$_3$ target. Sputtering occurred upwards onto a 7-inch diameter grounded electrode holding a 2-1/2-inch square substrate heater, mask, and substrates. The bias voltage in the plasma with respect to the positive ion was monitored. Slow deposition rates (5 to 10 A/min) corresponding to a target bias of -400 to -550 V at various substrate temperatures were investigated.

A standard high-vacuum pumping system was employed consisting of a 6-inch 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 4 x 10$^{-8}$ torr. Before the sputtering session, ultrahigh 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 18 to 22 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 800 to 1000°C in different ambients, viz. Ar, O$_2$, N$_2$ and O$_2$/N$_2$ mixtures for time varying between 5 minutes to 4 hours.

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 corresponds to a 1 x 10$^{15}$ atoms/cm$^3$ doping level. Before the film deposition, the wafers were thoroughly cleaned and etched in an HF buffer solution to strip off the SiO$_2$ layer. After cleaning, the substrates were blown dry by pre-purified nitrogen. Then the wafers were mounted on the substrate heater assembly and the assembly was then mounted in the vacuum system which was pumped down to the 10$^{-8}$ torr range. To test the ferroelectric properties of
BaTiO₃ films, a metal-insulator-semiconductor (MIS) structure was formed. Silicon wafers were 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 5 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 tin oxide (ITO) was also tried as the upper electrode.

2.2 Electrical measurements - Capacitance was measured as a function of voltage at 1 MHz characteristic frequency of a Boonton Model 71A capacitance meter. By superimposing a slowly varying (5 to 10 cycles/min) sine wave with an amplitude of 20 V onto the 1 MHz frequency, a continuous C-V curve was generated. The temperature of the sample was monitored by a Chromel-Alumel thermocouple attached to the sample. Polarization as a function of electric field was also measured at different frequencies (6, 60, 600 and 6 kHz) with a conventional Sawyer-Tower circuit and a Tectronix Model 454 oscilloscope was used to display the output.

The open circuit photovoltage for the MIS sandwich structure was measured using a Victoreen electrometer (Model 475B) which had an input impedance of 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 device remived. The photovoltage and photocurrent measurements were made at thermal equilibrium.
The structure of the target material and the films was analyzed by x-ray diffraction technique. A few films were also examined in a scanning electron microscope (SEM) at a magnification of up to 50,000X.

3. Results and Discussion

3.1 Structure - Figure 1 shows the typical x-ray diffraction pattern of the target material with the major peaks marked, (110), (111) and (200), which are characteristics of the pervoskite structure. The x-ray diffraction pattern for a good BaTiO₃ thin film sputtered on n-Si substrate at 550°C substrate temperature is shown in Figure 2. A good agreement between the two patterns shows that BaTiO₃ films with pervoskite-type structure, which usually have ferroelectric properties, are obtained on the silicon substrate. The two peaks near 61° and 69° are due to the silicon substrates. The structure of BaTiO₃ grown on a fused quartz substrate at 600°C substrate temperature is shown in Figure 3. Here again the agreement between the two patterns is good. These results thus show that tetragonal films of BaTiO₃ are grown on silicon and quartz substrates by r.f. sputtering. However, the half-width of each peak is broader than that of the target. This broadening is attributed to incompleteness of the crystalline structure, i.e., due to small grain size in the films. Scanning electron microscope study of BaTiO₃ films grown on n-silicon substrates at 500°C substrate temperature (Figure 4) consisted of grains of 150 to 250 Å size.

3.2 Ferroelectric properties - The capacitance was measured as a function of temperature at 1 MHz. Figure 5 shows the capacitance versus temperature plot for two different film thicknesses of BaTiO₃ sputtered on silicon at 550°C. Curve (a) is for a film of thickness about 0.3 μm. A broad transition in the region of
Figure 1. X-ray diffraction pattern of the target material.
Figure 2. X-ray diffraction pattern of BaTiO$_3$ film on silicon.
Figure 3. X-ray diffraction pattern of BaTiO$_3$ film on fused quartz.
Figure 4. Scanning electron micrograph of BaTiO$_3$ film deposited on n-Silicon at substrate temperature of 500°C, magnification 50,000X times and L = 0.2 μm.
Figure 5. Capacitance vs temperature for two different film thicknesses of BaTiO₃ on silicon deposited at a substrate temperature of 550°C. These samples also exhibit a counterclockwise hysteresis CV curve at 1 MHz.
120°C is seen. Curve (b) represents the variation of capacitance with temperature for a film of thickness of about 0.5 μm. A clear but broad peak is observed. Such smearing out of the dielectric constant as a function of temperature has been attributed to the small grain size. Another feature observed is that the maximum value of the capacitance increases as the thickness decreases and also the curve is broadened. The smearing out of the C versus T curve for BaTiO₃ can also be correlated with the film thickness. Since the film is, in fact, clamped to the substrate, thermal stresses developed due to the difference between the coefficients of thermal expansion of the films and substrate affect the dielectric constant with temperature. These stresses are reported to rise exponentially with decreasing thickness.

Polarization is a measure of the degree of ferroelectricity. The BaTiO₃ films were confirmed to be ferroelectric at room temperature from observation of the polarization-electric field (D-E) hysteresis loop by means of Sawyer-Tower circuit. Figure 6a shows a family of 60 Hz hysteresis loops obtained from a film deposited on silicon whose x-ray diffraction pattern was given in Figure 2. The polarization increases as the applied electric field is increased. The measured saturated remanent polarization (Pᵣ) was 0.45 μC/cm² and the coercive field (Eₐ) was 28 kV/cm for the lowest loop. Figure 6b shows the change in shape of the polarization versus electric field relationship for four different frequencies, 6, 60, 600 and 6 kHz, for the same MIS device tested for Figure 5a.

The low Pᵣ and high Eₐ compared to the bulk material has been shown to be attributed to the small grain size of the films. The increase in Eₐ with decreasing thickness is possibly due to stresses exerted by the substrate because of the differential thermal expansion between the film and the substrate.
Figure 6(a). P-E hysteresis loops for a 60 Hz sine wave for three amplitudes of 3.9, 6, and 8 V. \( L = 0.5 \, \mu \text{m}, \, E_c = 28 \, \text{kV/cm}; \, P_f = 0.45 \, \mu \text{C/cm}^2 \) for lowest loop.

(b). P-E hysteresis loops for sine waves with an amplitude 4 V, frequencies 6, 60, 600 and 6000 Hz. The 6 Hz curve has a visibly counterclockwise sense. \( L = 0.3 \, \mu \text{m}, \, E_c = 86.6 \, \text{kV/cm} \) and \( P_f = 2.2 \, \mu \text{C/cm}^2 \) for 60 Hz.
3.3 Capacitance-voltage and memory characteristics - The capacitance-voltage measurements were employed to study the memory switching properties. When tunneling or ferroelectric effect becomes important, the C-V curve opens up into a hysteresis loop with a clockwise or counterclockwise sense. Figure 7 shows the typical C-V curve obtained for BaTiO$_3$ film on silicon, whose x-ray diffraction pattern was given in Figure 2. The counterclockwise sense of the curve with a hysteresis window of about 9 V clearly shows the ferroelectric effect in the film.

Figure 8 shows a set of C-V curves obtained for the same device of Figure 7. After recording the original C-V curve a set of curves were obtained by successively applying positive write pulses with increasing duration and amplitude until the device has switched to a flat-band position near the positive bias end. Then the device was switched to the negative direction by successively applying negative bias pulses. Thus, this particular device can be effectively switched to the positive end by approximately +25 V; a 50 msec pulse and a -30 V pulse is needed to switch it to the negative end.

3.4 Photovoltaic properties - A device 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 increased with light intensity, whereas the photo-emf was a function of intensity at low intensities, but saturated at higher levels. The relation between photo-emf and intensity is shown in Figure 9. The results obtained for a particular device is typical of the others. The unpoled device gave lower photovoltage as compared to the poled ones. As the poling voltage was increased the photovoltage increased until the
Figure 7. Typical ferroelectric hysteresis curve for BaTiO$_3$ film deposited on silicon at substrate temperature of 550°C.
Stress Sequence (volts/msec)
1) Original
2) -20, 10
3) -25, 10
4) -30, 10
5) +20, 10
6) -25, 10
7) +15, 10
8) +15, 50
9) +15, 100
10) +20, 10
11) +20, 100
12) +25, 10
13) +25, 50
14) +25, 100

Normalized capacitance ($C/C_0$)

$V_G$ - Gate Voltage (in volts)

Figure 8. C-V memory switching characteristics of BaTiO$_3$ films deposited on silicon at substrate temperature of 550°C, 1 MHz.
Figure 9. Intensity (mw/cm²).

Photovoltage (V/cm)

- #3 poled
- #7 poled
- #3 unpoled and annealed
- #7 unpoled and annealed

Intensity (mw/cm²)
remanent polarization saturated. Once the device was poled, it remained in that state. Annealing of the device in oxygen atmosphere, however, reduced the photovoltage output. Table 1 summarizes the saturated photo-emf results obtained for poled, unpoled, and annealed devices at various substrate temperatures. The photovoltage output was lowered when as-evaporated In$_2$O$_3$ was used as the top electrode. This is probably due to the nonstoichiometric nature of In$_2$O$_3$ film. It is known that In$_2$O$_3$ on thermal evaporation dissociates to lower suboxide and/or indium metal, thus resulting in nonstoichiometry.

From the present work and the reported literature, to obtained 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 results for BaTiO$_3$ films sputtered at 660°C substrate temperature are summarized. The device was polarized in either direction by applying a high voltage (40 V for a maximum of one minute). The photovoltage changes for the first few cycles are given. As seen though the polarity of the photo-emf is the same in 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 device is polarized in the negative direction (i.e., the upper electrode is poled negative).

Few of the devices were fabricated with ITO as the top electrode. In recent years, ITO films are widely used in the field of solar energy. The ITO films in the present case were prepared by thermal evaporation. However, this material dissociates on thermal evaporation. The as-evaporated films were brownish in color, but became transparent when oxidized in air. For example, the as-evaporated films were highly absorbing in nature and had
Table 1

BaTiO$_3$ on Silicon
Photovoltaic Output at Room Temperature for Various Deposition Conditions†

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

†Values are for polarization in one direction. The photo-emf developed on upper electrode 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$_2$O$_3$ contact.
Table 2

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

<table>
<thead>
<tr>
<th>No. of Cycles</th>
<th>Saturation Photo-emf (mV) (Upper Electrode Poled Positive, 40 V)</th>
<th>Saturation Photo-emf (mV) (Upper Electrode Poled Negative, 40 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-70</td>
<td>-185</td>
</tr>
<tr>
<td>2</td>
<td>-68</td>
<td>-189</td>
</tr>
<tr>
<td>3</td>
<td>-88</td>
<td>-190</td>
</tr>
<tr>
<td>4</td>
<td>-94</td>
<td>-170</td>
</tr>
<tr>
<td>5</td>
<td>-94</td>
<td>-168</td>
</tr>
</tbody>
</table>
only 20 percent transmission at 600 nm. However, when oxidized, these films became highly transparent with 70 percent transmission at 600 nm.

Figure 10 shows the results obtained for a device with ITO as the top electrode, which was oxidized in argon atmosphere for 2 hours at 250°C. The virgin device gave a very low photovoltage output, with negative polarity, but when the device was polarized (27 V, 5 sec) in the positive direction, the photovoltage output was positive and the magnitude increased. It then slowly decayed with time to a lower value. On applying a negative voltage pulse (-27 V, 5 sec), the photovoltage output was negative, but here also it decayed with time and became positive. This was true for the next ten successive voltage pulses.

The sputtered films on fused quartz substrate were of white color, transparent, of good adherence and uniform over a considerable area. As shown in Figure 3, the films gave a crystalline pattern in agreement with the target material. Further studies on other properties of BaTiO₃ films produced are in progress.

4. Conclusions

In summary, ferroelectric films of BaTiO₃ have been successfully deposited by r.f. sputtering in 10 percent O₂/90 percent Ar mixture at substrate temperature above 500°C. The x-ray diffraction and SEM analyses indicate that films with pervoskite-type structures are obtained on silicon and quartz substrates. The D-E hysteresis loops, the clear dielectric peak and counterclockwise sense of the C-V curves, confirm the ferroelectricity of the r.f. sputtered BaTiO₃ films. The low Pr and high Ec values are attributed to the small grain size. The memory switching characteristics of the MFS devices are presented.

This work also reports the first observation of the high photovoltaic (24 x 10³ V/cm) effect in thin films of BaTiO₃.
Figure 10. Decay of photo-emf with time after the polarization was switched.
(a) negative voltage pulse (27 V) applied 
(b) positive voltage pulse (27 V) applied.

Time in Minutes

Potential (mV)
produced by r.f. sputtering. At present, the source of switchable emf is not known, although it appears to be related to the spontaneous polarization of the material showing some barrier-like qualities. From this work, the ferroelectric BaTiO$_3$ film is expected as a promising candidate for the photovoltaic-ferroelectric-semiconductor nonvolatile memory. The improvement in the device characteristics is in progress.