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INDIRECT AMPLIFICATION OF THE PYROELECTRIC SIGNAL IN $Pb(Zr,Ti)O_3$ THIN FILMS BY THE PHOTO-GENERATION OF CARRIERS IN THE Si SUBSTRATES

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An amplification of near three orders of magnitude was observed in $Pb(Zr,Ti)O_3$ (PZT) thin films deposited on Pt/Si substrates when the Si substrate is included as an impedance in series with the PZT capacitor. The effect is present only at wavelengths below 1100 nm, where the incident light can be absorbed in the Si substrate with generation of free carriers. These carriers in turns modulate the internal electric field inside the ferroelectric layer leading to a much larger variation of the polarization compared to the one generated only by the temperature variation. This fact leads to a considerable enhancement of the pyroelectric signal. The finding can be useful in designing pyroelectric detectors with enhanced characteristics for visible and near infrared region of the electromagnetic spectrum.

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1. Introduction

Pyroelectric detectors are functioning based on the pyroelectric effect, meaning the variation of the spontaneous polarization with the temperature of the active element [1]. They are used in a large variety of applications, from intruder alarms to thermal imaging and infrared (IR) spectroscopies [2-6]. In most cases the pyroelectric active element consist of a capacitor manufactured from a single crystal (e.g. $LiNbO_3$ or $LiTaO_3$) or from a ceramics (e.g. $Pb(Zr,Ti)O_3$-PZT or $(Ba,Sr)TiO_3$-BST) [7-9]. However, integration with Si-based electronics and the miniaturization of the pyroelectric devices for IR detection requires the use of thin films that should be deposited directly on Si wafers. Thin films from materials with pyroelectric properties such as ferroelectric PZT or polar wide gap semiconductors such as ZnO or AlN can be obtained on Si substrate by various techniques, such as sol-gel or radio-frequency (RF) sputtering [10-12]. In some cases the Si substrate is removed after processing the pyroelectric elements [12]. The removal however, can limit the operation frequency range to low modulation frequencies (below 100 Hz) of the incident IR beam [13].

Here we show that the maintaining of the Si substrate beneath the pyroelectric element can lead to higher operation frequencies, well above 100 Hz. Moreover, an unusual amplification of the pyroelectric signal occurs if the IR light has wavelengths below 1100 nm. This effect is observed only when the Si substrate is included in the measuring circuit of the pyroelectric signal. Therefore, the amplification of the pyroelectric signal is attributed to the photogenerated carriers in the Si substrate which, in turns, modulated the electric field inside the pyroelectric element. This leads to a polarization variation that adds to the one produced by the temperature variation due to the incident IR beam. The amplification can be as large as of three orders of magnitude.

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2. Experimental

PZT thin films with Zr/Ti ratio of 20/80 were grown on Pt/Si (nominal Pt(100 nm)/TiO_2(15 nm)/SiO_2(450 nm)/Si(500 μm)) substrates by sol-gel method (details can be found in ref. [14]). The precursor solution was spin-coated on the substrate at 3000 rpm for 20 s. The film was the pyrolised at 200 ^{0}C for 2 minutes and at 400 ^{0}C for 4 minutes in order to eliminate the organic residues. The spin-coating/pyrolisis sequence was repeated several times, until the desired film thickness was achieved (usually 10 times for a film thickness of about 500 nm). At the end the film was crystallized by conventional thermal annealing in air, at 600 ^{0}C for 30 minutes. The X-ray diffraction analysis has revealed only the presence of the perovskite phase, with random crystalline orientation. As expected, the films are polycrystalline, with a thickness of about 450 nm estimated from scanning electron microscopy (SEM) photographs (see Fig. 1).

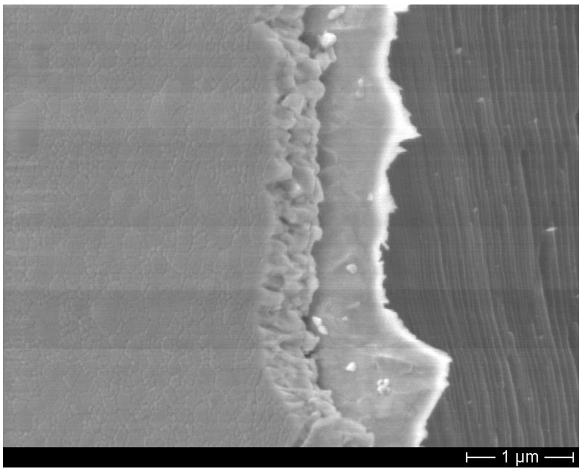

Fig. 1 SEM photograph of the PZT film deposited by sol-gel on Pt covered Si wafer.

Top Pt electrodes with area of 0.275 mm^2 were deposited for electric and pyroelectric measurements. The presence of ferroelectric polarization was evidenced by performing hysteresis and capacitance-voltage (C-V) measurements using a TF2000 ferritester from AixACCT and an impedance/gain analyzer HP 4194A, respectively. Current-voltage (I-V) measurements were also performed in order to estimate the electrical conductance of the active pyroelectric element.

For pyroelectric measurements, the entire Pt/PZT/Pt/Si wafer was glued with silver (Ag) paste on an Au-covered alumina ceramic plate. A laser diode of 800 nm wavelength was used as IR source. The power density from the IR source was estimated to about 1200 W/m^2. The light beam was modulated with a mechanical chopper in a frequency range between 15 and 500 Hz. The measurements were performed in the voltage operation mode, which implies that the ferroelectric capacitor (the active IR element) is connected to the gate electrode of a JFET transistor [15]. Two connection possibilities were used for the pyroelectric active element: 1) the gate contact was connected to the top Pt electrode and the ground was connected to the bottom face of the Si substrate, such that the entire Pt/Si/Ag(Au) stack is included in the measurement circuit (see Fig.2a); 2) the gate contact was connected to the Pt top electrode and the ground to the bottom Pt electrode, leaving the Si substrate only as a mechanical support for the PZT capacitor, without being included in the measurement circuit (see Fig.2b). The signal was recorded from a load resistance of 100 kΩ connected between the FET's source contact and the ground by using a lock-in amplifier model SR830.

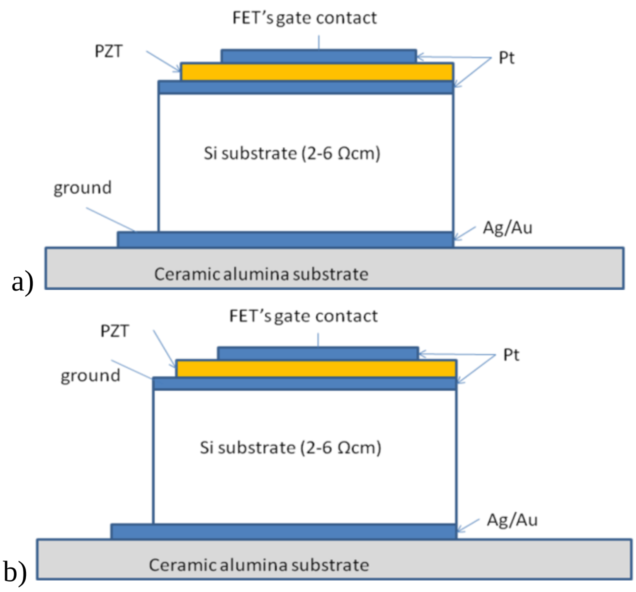

Fig. 2 a) connection with the Si substrate included in the measurement circuit, considering the entire Pt/Si/Ag/Au stack as bottom electrode for the PZT film; b) connection without the Si substrate included in the measurement circuit (ground contact on the Pt layer deposited on Si, gate contact on the top Pt electrode).

3. Results and discussions

The results of the pyroelectric measurements are presented in Fig.3. The dips occurring at 50 Hz and 100 Hz are due to the two Notch filters used in the lock-in amplifier in order to reject the noise induced at these frequencies by the power lines. One can see in Fig. 3 that the signal magnitude is very different for the two situations, with or without the Si substrate included in the measuring circuit. If only the PZT capacitor is connected to the gate of the FET the signal is with almost three orders of magnitude lower than for the case when the Si substrate is also included in the measurement circuit. As regarding the frequency dependence, one can observe that when the Si substrate is not included in the measuring circuit the dependence is typical for a pyroelectric detector, with the signal decreasing as the chopping frequency of the IR beam increases [2]. This case is typical when $\omega\tau_T$>>1 and $\omega\tau_e$>>1. Here ω is the pulsation of the incident IR radiation, τ_T is the thermal time constant, and τ_e is the electrical time constant. The first condition is fulfilled because τ_T is very large (of the order of 100 seconds) due to the thick Si substrate, introducing a large thermal capacitance in the thermal circuit [15]. In the case of polycrystalline PZT thin films the τ_e can be also large enough to fulfill the condition $\omega\tau_e$>>1. The electrical measurements performed on the ferroelectric capacitor (see later on) have shown that this has a capacitance of about 1.1 nF and an electrical conductance of about 10^{-9} S, leading to an electrical time constant of the order of 1 second. It means that at 10 Hz modulation frequency the condition $\omega\tau_e$>>1 is fulfilled. The frequency dependence seems to change when the Si substrate is included in the measuring circuit. The signal has a small increase at low frequencies and then, above 60 Hz becomes almost constant. This can be due to a change in τ_e, considering that the equivalent circuit is more complicated when the entire substrate is included as impedance in the gate circuit (see Fig. 2a).

The unusual amplification of the signal when the Si substrate is included in the circuit can be explained assuming that part of the incident light penetrates into the Si substrate and generates free carriers by band-to-band absorption. This is very possible, considering that the wavelength of the incident IR beam is of 800 nm, where the absorption coefficient in Si is of 850 cm^{-1}.

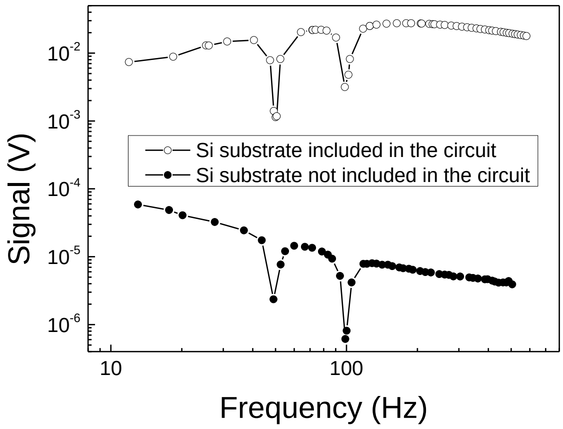

Fig. 3 Frequency dependence of the pyroelectric signal measured with and without the Si substrate included in the measurement circuit.

In order to check this, a piece of 1.5 cm^2 of Pt/Si substrate was used as photoconductive element, using a standard set-up for photoconductivity measurements (see Fig.4a). The same IR source was used, with a load resistance of 100 kΩ to collect the signal in modulated light. The obtained result is presented in Fig.4b.

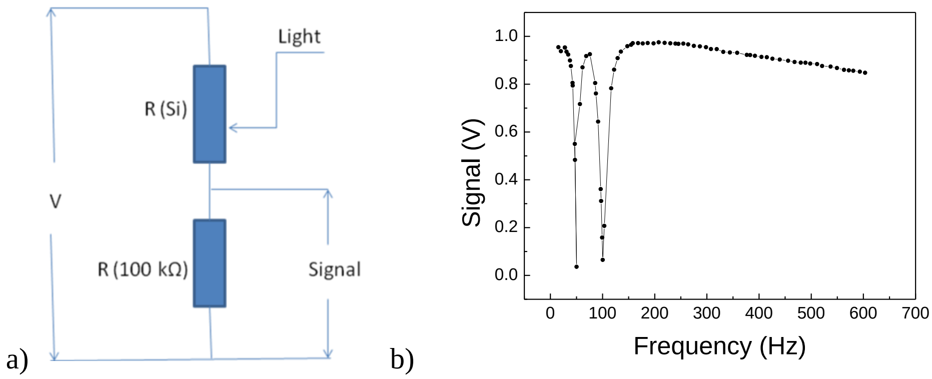

Fig. 4 a) set-up for photoconductivity measurement on Pt/Si substrate; b) the frequency dependence of the photoconductive signal obtained from the Pt/Si substrate.

A large signal is obtained, showing that part of the light with 800 nm wavelength penetrates the 100 nm thick Pt electrodes and is absorbed into the Si substrate where generates free carriers by band-to-band absorption. The density of the photogenerated carriers in Si was estimated from the photoconductivity measurements shown in Fig. 3. A value of about $8x10^{20}$ $m^{-3}s^{-1}$ is obtained, if the illumination would be continuous. However, the illumination is modulated. The amount of free carriers generated during half-period, when the Pt/Si substrate is exposed to light, can be estimated to about $8x10^{19}$ m^{-3} for a modulation frequency of 10 Hz, and to about $1.5x10^{18}$ m^{-3} for a modulation frequency of 500 Hz. It is assumed that only the carriers from the screening length of the Si substrate (the Debye length) are accumulating on the Pt electrode of the PZT film [16]. For a non-degenerate Si substrate, with a carrier concentration in the range of 10^{22} m^{-3}, the Debye length is of the order of 40 nm at room temperature. The charge that accumulates on the electrodes of the PZT capacitor will be of about 0.2 pC at a modulation frequency of around 10 Hz. Considering that the measured capacitance of the 450 nm thick PZT layer is of about 1.1 nF (see Fig.5a), it results an internal electric field of about 4-5 V/cm. Such a field can produce a variation of the ferroelectric polarization of the order of 10^{-4} $\mu C/cm^2$, as suggested by the hysteresis loop presented in Fig.5b.

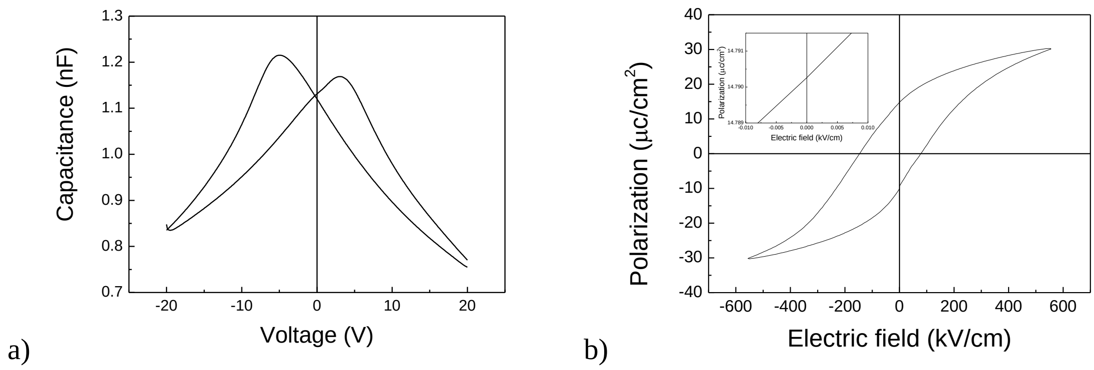

Fig. 5 a) the C-V characteristic of the PZT capacitor used as pyroelectric element on Pt/Si substrate; b) the hysteresis loop obtained for a PZT film deposited on Pt/Si substrate. The inset shows the polarization variation at low electric fields, around zero volts/cm.

The polarization variation induced by the temperature change ΔT due to the incident IR light can be estimated considering the signal recorded without the Si substrate included in the measurement circuit. One can assume that this signal is related only to the pyroelectric effect in the PZT layer. A value of about $4\text{x}10^{-4}$ C/m^{2}K will be considered for the pyroelectric coefficient *p*, as for a bulk ceramic sample [17-19]. The temperature variation *ΔT* at a modulation frequency of around 10 Hz can be calculated from the equation $S = \frac{pA\omega\Delta T}{G_e}$ [20], where *A* is the electrode area (0.275 mm^2), and G_e is the electrical conductance of the PZT capacitor. This was estimated to about 10^{-9} S from I-V measurements at low voltages. Considering *S* of about 60 μV (see Fig. 3, the signal without the Si substrate included in the measuring circuit), then the temperature variation is of the order of 10^{-6} ^{0}C. Knowing that the pyroelectric coefficient is $p = \frac{\Delta P}{\Delta T}$ then the polarization variation *ΔP* is of the order of 10^{-7} μC/cm^2, which is about three orders of magnitude lower than the polarization variation produced by the photogenerated carriers in the Si substrate. This result is in good agreement with the experimental data presented in Fig.3.

The effect was observed not only for PZT thin films but also for PZT-$BiFeO_3$ multilayers, as well as for other polar materials used for pyroelectric detection such as ZnO or AlN. In all cases the signal recorded with the Si substrate included in the measuring circuit is with orders of magnitude larger than for the case when the Si substrate is not included in the circuit (see Fig. 6).

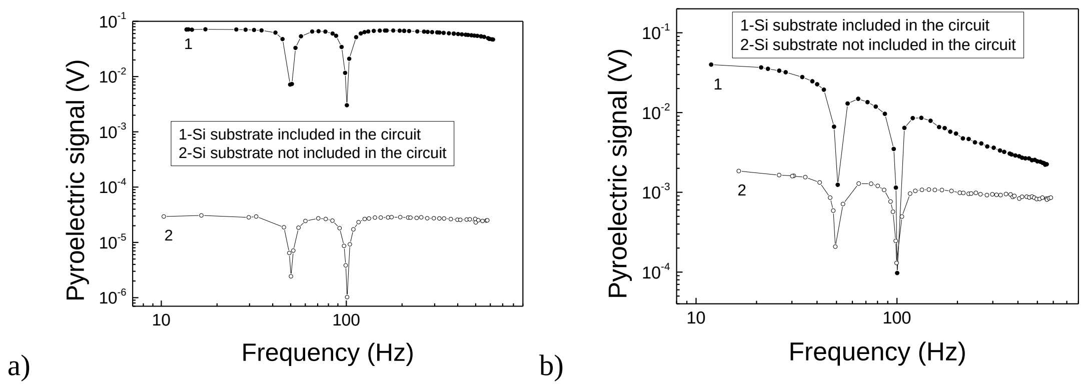

Fig. 6 Frequency dependence of the pyroelectric signal, with and without the Si substrate included in the measuring circuit, for a PZT-$BiFeO_3$ multilayer (a) and for AlN thin film (b). The PZT-$BiFeO_3$ multilayer was deposited by sol-gel. The AlN film was deposited by radio-frequency (RF) sputtering. The Si substrate was of the same quality as for the PZT films shown in Fig. 1.

Therefore, the pyroelectric signal produced by the pyroelectric layer can be “amplified” with orders of magnitude when the incident light has wavelengths that can be absorbed, with generation of free carriers, in the Si substrate. The amplification can be useful for spectroscopic methods in the near infrared range, simplifying the electronics related with the processing of the pyroelectric signal. One can also assume that, by changing the material for the substrate, the wavelength domain of this indirect amplification can be changed depending on the band-gap of the semiconductor material used as substrate for the pyroelectric film. This hypothesis needs further studies.

4. Conclusions

Pyroelectric properties of PZT films deposited by sol-gel on Pt-covered Si wafers were investigated. It was found that the pyroelectric signal is strongly amplified if the Si substrate is included in the measuring circuit as serial impedance to the active pyroelectric element represented by the ferroelectric capacitor. The observed phenomenon occurs only at wavelengths where carriers are photogenerated into the Si substrates. These carriers accumulates on the ferroelectric capacitor, producing a variable electric field that in turns produces a polarization variation in phase with the one produced by the temperature variation induced by the light beam incident on the pyroelectric element. This finding can be useful in designing pyroelectric detectors with enhanced detection properties for the near-infrared part of the electromagnetic spectrum.

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