Pyroelectric, piezoelectric, and photoeffects in hydroxyapatite thin films on silicon

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Hydroxyapatite (HA) is the major component of bone and is used in artificial form in many biomedical applications. It was once believed to have a centrosymmetric crystal structure. In theoretical and experimental studies published in 2005, it was shown to have a monoclinic $P2_1$ structure. In the work reported here, 500 nm films of HA were spin-coated on silicon wafers. The materials were *not poled.* They had a nonuniform polarization distribution and exhibited pyroelectricity, piezoelectricity, and photoeffects. Structures of this type may have a number of technological applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3571294]

As a natural material, hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (HA) forms 60%–70% of the mass of human and animal bone.[1] In artificial form, it is widely used in reconstructive orthopedic and dental surgery, both as a massive filling of bone gaps and as a surface coating.[2] Recently, its electrical properties have become of interest because of the possibility of the electrical manipulation of surface charge.[3] A piezoelectric effect was observed in bone by Fukada and Yasuda in 1957.[4] A pyroelectric effect was found by Lang in 1966.[5] In both cases, the effects were attributed to the polar collagen component of bone because HA was believed to be isostructural with apatite, a centrosymmetric structure. Recently, theoretical and experimental studies have shown that HA has a noncentrosymmetric monoclinic structure, $P2_1$.[6,7] A pyroelectric surface charge in electrically poled HA ceramics[8] and a very weak shear piezoelectric effect in unpoled HA ceramic[9] have been observed. A detailed study of size and shape related dielectric properties of HA nanoparticles was published recently.[10] We report here the experimental measurements of *strong* pyroelectricity and piezoelectricity in *unpoled* HA thin films.

The set of samples of HA on silicon substrates was prepared as follows. Phosphorus pentoxide [P_2O_5, Sigma-Aldrich, 98%] and calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot (H_2O)_4$, Sigma-Aldrich, 99%] were dissolved individually in absolute ethanol (CentralChem, 99.8%). These two solutions were combined slowly in a Ca/P molar ratio of 1.67. The mixture was continuously stirred and heated at 60 °C for 1 h. The resulting sol was spin-coated on the (100) surfaces of n-doped silicon wafers. The wafers were dried for 1–2 h at 200 °C, then calcined at 700 °C for 1 h with heating and cooling rates of 5 °C min^{-1}. The thickness of the HA layer was about 500 nm. An 80-nm thick layer of amorphous silica was formed between the HA and the Si wafer during the calcinations. The phase purity of the resulting films was checked by glancing X-ray diffraction using Cu $K\alpha$ radiation. The diffraction pattern was in excellent agreement with the literature (Fig. 1).[6,11] The ratio of the peaks (300)/(002) was close to unity in contrast to the value of 1.8 observed in completely random polycrystals. This high proportion of intensity of the reflection from (002) indicates a significant amount of out-of-plane *c*-axis orientation in the film. Atomic force microscopy and scanning electron microscopy (SEM) studies showed a crystallite size in the range of 70–100 nm. An 80-nm-thick Au/Pd electrode was sputtered on the top surface of the HA and the silicon substrate served as a bottom electrode.

A set of HA samples on glass substrates was prepared in the same manner except that the glass was first sputtered with a 10 nm interlayer of Ti for increasing the adhesion to the substrate. The Ti was covered with a 40 nm layer of Pt. X-ray analysis of the HA/glass samples showed the presence of poorly crystalline HA. A Au/Pd electrode was sputtered on the top surface and electrical contacts were made to the Pt layer which served as a bottom electrode.

None of the HA samples was electrically poled.

In the pyroelectricity experiments, a diode laser (Model HL25, Lisa Tech, Germany) with power=8.1 mW, wavelength=685 nm and beam diameter=1 mm was used.

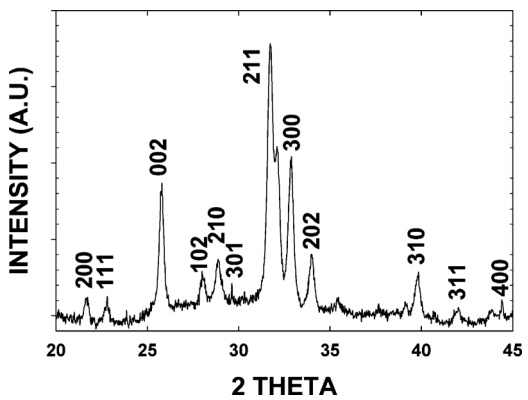

FIG. 1. X-ray diffraction pattern of HA.

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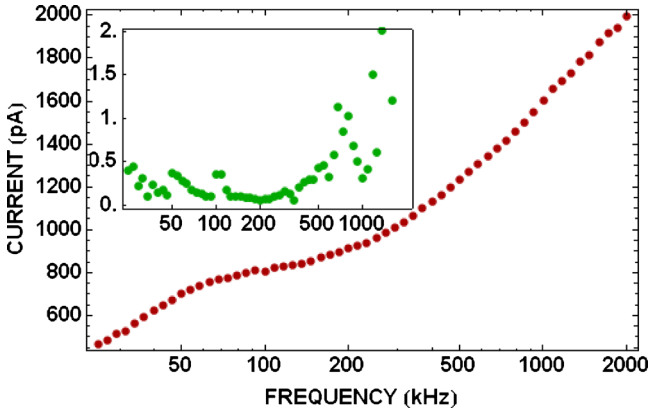

FIG. 2. (Color online) Amplitude of pyroelectric current in LIMM measurements. Main figure: Ha/Si. Inset: HA/glass.

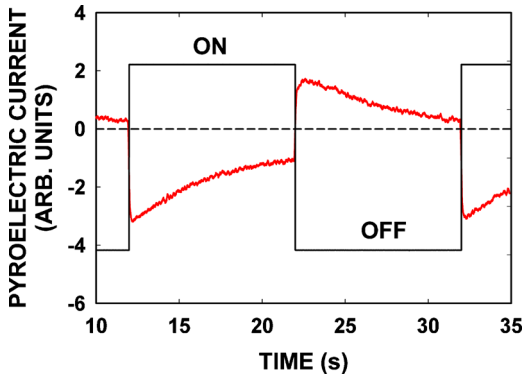

FIG. 3. (Color online) Pyroelectric current measured with laser on-off cycle at 0.05 Hz.

The Au/Pd electrodes were partially transparent with an absorbance of 72%, a transmission of 22% and a reflectance of 6% at the 685 nm laser wavelength.

In the first set of experiments, the samples were examined using the laser intensity modulation method (LIMM).[12] This is a technique for determining the spatial distribution of polarization in the thickness direction of a sample. In this method, a laser beam that is modulated in intensity sinusoidally impinges on the top electrode. The energy of the beam is absorbed and heat diffuses into the sample in the form of temperature waves. The waves are attenuated in amplitude and phase-shifted as they travel into the material with low frequency waves penetrating to a greater depth; higher frequency ones to a shallower depth. The temperature waves excite a pyroelectric current whose real and imaginary components are measured and the polarization distribution is calculated by solving a Fredholm integral equation of the 1st kind.[13] The pyroelectric current was measured with a current amplifier with a 10^6 V A^{-1} gain (Model HCA-2M-1M-C, Femto Messtechnik, Germany) and a 200-MHz radio-frequency lock-in amplifier (Model SR844, Stanford Research, USA). The amplitudes (computed from the real and imaginary components) of the pyroelectric currents for a frequency range from 25 kHz to 2 MHz are shown in Fig. 2. Corrections were made for the attenuation and phase shift in the current amplifier at frequencies close to its bandwidth. All of the measurements were replicated on three samples of each type. The temperature increase due to the laser beam absorption could not be measured but theoretical calculations indicate that it was of the order of microdegrees.[14] The currents measured on the HA/Si samples were of the order of nanoamperes whereas the currents observed on the HA/glass samples were less than a picoampere. This confirmed that the HA/Si samples contained oriented dipoles and the larger magnitudes of the current at high frequencies showed that the dipolar orientation was greater near the free surface. The very small currents measured on the HA/glass samples confirmed their poor crystallinity. Consequently, no further measurements were made on the HA/glass samples.

A true pyroelectric signature was obtained by turning the laser beam on and off at a frequency of 0.05 Hz (Fig. 3). The absorbed laser energy raised the temperature of the sample slightly above ambient. When the laser beam was turned on, a negative pyroelectric current was produced which relaxed toward zero as the sample temperature returned to the average. The opposite effect was observed when the laser beam was turned off. However, the current with the laser off approached zero more rapidly than that with the laser on. This observation was confirmed by reducing the frequency to 0.005 Hz. The current with the laser on clearly did not relax to zero but reached a constant nonzero value. However, when the laser was turned off, the current did relax to zero (Fig. 4). Because of the partial transparency of the electrode and the HA, some laser light reached the silicon and excited a definite *photoeffect*. The magnitude of the photocurrent was about 3 μA W^{-1}. A similar magnitude photocurrent was observed with a silicon wafer having no HA deposit.

Two additional experiments were conducted to confirm the polar character of the HA/Si. In the first, a piezoelectric measurement was made by pressing and releasing a Teflon rod against the sample at a frequency of 0.1 Hz. Figure 5 shows the cyclic pressure and the piezoelectric charge produced. A d_{33} coefficient of 16 pC N^{-1} was measured, a value of about half of that of fully poled polyvinylidene fluoride polymer (PVDF). The setup was calibrated with a crystal of $LiNbO_3$ and with PVDF. However, the technique can underestimate the d_{33} coefficient if the thickness/area ratio of the sample is small.[15] In a second experiment, the pyroelectric current was determined by means of a Byer Roundy experiment[16] (Fig. 6). The temperature of the sample was increased and decreased at a rate of 1 °C min^{-1} over a temperature range from 30 to 80 °C. When the temperature was increasing, a negative current was recorded. A positive current was observed when the temperature was decreasing and the current was zero when the temperature was constant. The

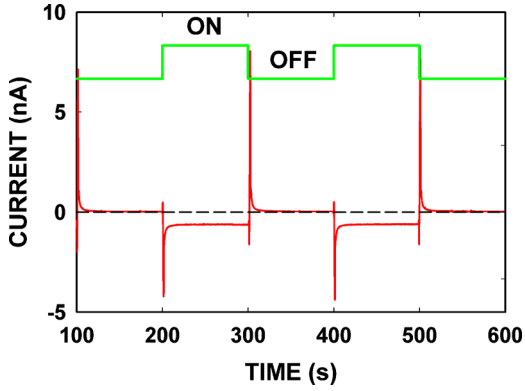

FIG. 4. (Color online) Pyroelectric current measured with laser on-off cycle at 0.005 Hz.

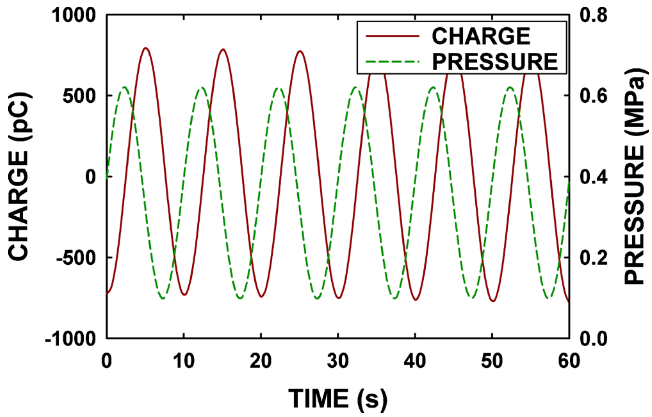

FIG. 5. (Color online) Piezoelectric strain measurement of HA film on Si substrate.

equation, $I = pA\,dT/dt$, was used to calculate the pyroelectric coefficient. Here I=pyroelectric current, p=pyroelectric coefficient, A=electrode area, and dT/dt=rate of change in temperature. A pyroelectric coefficient of about 12 $\mu C\ m^{-2}\ K^{-1}$ was found. This is about 1/3 of the coefficient of fully poled PVDF.

Tofail *et al.*[8] have found that the dipole of HA is the hydroxyl (OH) ion, which lies along the crystallographic *c*-axis within the tunnel formed by phosphate (PO_4) tetrahedra. Assume that, in an arbitrarily chosen tunnel, there are two OH ions pointing in the same directions. In an adjacent tunnel, the OH ions could point in a parallel direction or in an antiparallel one. The antiparallel arrangement has been found to be in the lowest energy state.[6] The energy differences between these phases were small (a few kilojoules per mole) thus allowing either a nonpolar to polar phase transition[8] or a stabilization of the polar phase.[6,17] We believe that the high-temperature calcination crystallized the HA film on silicon and converted most of the OH pairs to a parallel configuration. Thus the HA develops a domain structure with randomly oriented dipoles. Upon cooling, sufficient domains reorient in polarity so as to result in a net polar structure.

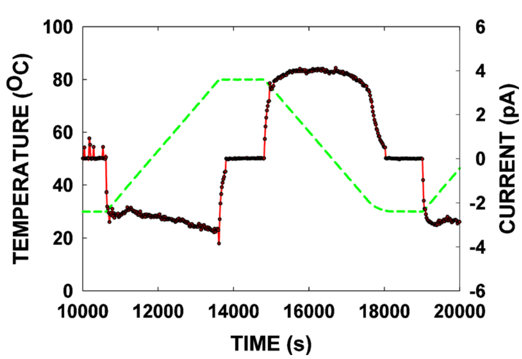

FIG. 6. (Color online) Byer–Roundy experiment.

This is due to the crystalline character of the silicon substrate and texturing. The HA films on glass samples were insufficiently crystallized to show any polar behavior.

The photocurrent is caused by the silicon alone. The energy of the 685 nm laser photons is 1.81 eV, which is significantly greater than the 1.11 eV band gap of silicon. HA has a band gap of 3.9 eV, much larger than the photon energy and consequently could not contribute to the photocurrent.[18] The n-doped silicon is centrosymmetric and cannot give pyroelectric or piezoelectric effects. Thus the origins of the two classes of effects are unique to the two materials in the sample structure. The source of the photocurrent in the silicon is under current investigation.

In addition to its scientific interest, the HA/Si materials may have useful technological applications as pyroelectric/photoeffect structures. Uses might include the following: large area position sensitive devices, photovoltaic driven piezoelectric transformers, power sources for laptops and other electronic devices, and solar energy conversion.

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