

# Photovoltaic effect in thin $\text{Bi}_{12}\text{GeO}_{20}$ films

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A photovoltaic effect has been discovered in textured thin films of  $\text{Bi}_{12}\text{GeO}_{20}$ . The component  $K_{14}$  of the photovoltaic-current tensor is of the same order of magnitude as in single crystals.

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Crystals lacking an inversion center exhibit a photovoltaic effect, which is described by a third-rank tensor.<sup>1,2</sup> In high-resistivity insulators this effect gives rise to a photorefraction. The photovoltaic effect has been detected and studied in single crystals. Particularly interesting here are crystals with the sillenite structure (symmetry space group 23), which have found applications in electro-optic devices: Pockels space-time readout optical modulators. The photovoltaic effect was first discovered in single crystals of this group in  $\text{Bi}_{12}\text{SiO}_{20}$  (Ref. 3), and it was later found in<sup>4,5</sup>  $\text{Bi}_{12}\text{GeO}_{20}$  and  $\text{Bi}_{12}\text{TiO}_{20}$ . In this letter we report observation of a photovoltaic effect in thin  $\text{Bi}_{12}\text{GeO}_{20}$  films.

The experiments were carried out with  $\text{Bi}_{12}\text{GeO}_{20}$  films synthesized by reactive sputtering of a composite bismuth-germanium target in an apparatus with a planar magnetron. An x-ray analysis of the resulting bismuth germanate films carried out with a URS-50I diffractometer showed that it was possible to produce, depending on the substrate temperature  $T_s$ , amorphous films ( $T_s = 50\text{--}150^\circ\text{C}$ ), fcc polycrystalline films ( $T_s = 200\text{--}400^\circ\text{C}$ ), bcc polycrystalline films ( $T_s \geq 450^\circ\text{C}$ ), and textured films ( $T_s \geq 500^\circ\text{C}$ ). For the measurements we selected textured films of bismuth germanate synthesized at  $T_s = 600^\circ\text{C}$ . The use of sapphire as a substrate made it possible to

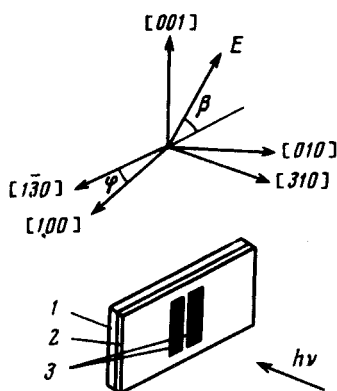


FIG. 1. Experimental geometry. 1—Sapphire substrate; 2—bismuth germanate film; 3—aluminum electrodes.

produce  $\text{Bi}_{12}\text{GeO}_{20}$  films oriented in the (310) plane. The films were  $1.5\text{--}2\text{ }\mu\text{m}$  thick.

The experimental geometry (Fig. 1) differs from that of Refs. 3–5, where the current was measured in the light propagation direction. We deposited aluminum electrodes on the (310) surface of the film. The gap between the electrodes was 0.1 mm. The photovoltaic current was measured with a V7-30 electrometer in the  $[\bar{1}\bar{3}0]$  direction. The film was illuminated with a linearly polarized beam from a He-Cd laser ( $\lambda = 441.6\text{ nm}$ ). The polarization plane of the beam was rotated by a quartz half-wave plate; this rotation changed the light intensity by no more than 2%. All the measurements were taken at room temperature.

For this particular experimental geometry, we can write the following expressions for the current density, taking into account the  $\text{Bi}_{12}\text{GeO}_{20}$  symmetry group:

$$j[\bar{1}\bar{3}0] = j[100] \cos \phi - j[010] \sin \phi, \quad (1)$$

$$j[100] = \frac{1}{2} \alpha K_{14} I \sin \phi \sin 2\beta, \quad (2)$$

$$j[010] = -\frac{1}{2} \alpha K_{14} I \cos \phi \sin 2\beta, \quad (3)$$

The measured photovoltaic current is therefore

$$j[\bar{1}\bar{3}0] = \frac{1}{2} K_{14} \alpha I \sin 2\beta \sin 2\phi, \quad (4)$$

where  $\alpha$  is the light-absorption coefficient,  $\beta$  is the angle between the light-polarization plane and the direction  $[\bar{1}\bar{3}0]$ ,  $\tan \phi = 1/3$ ,  $K_{14}$  is a component of the photovoltaic tensor, and  $I$  is the light intensity.

Figure 2 shows the experimental dependence of the photovoltaic current  $j$  on the angle  $\beta$  according to (4). Using the experimental values  $\alpha = 30\text{ cm}^{-1}$ ,  $I = 5\text{ W/cm}^2$ , and  $d = 1.5\text{ }\mu\text{m}$  (the film thickness), we find  $K_{14} \approx 1 \times 10^{-9}\text{ A cm/W}$ , in approximate agreement with the values of  $K_{14}$  for single crystals with the sillenite structure:

for  $\text{Bi}_{12}\text{SiO}_{20}$ ,  $K_{14} \approx 0.5 \times 10^{-9}\text{ A cm/W}$  (Ref. 3),

for  $\text{Bi}_{12}\text{GeO}_{20}$ ,  $K_{14} \approx (3\text{--}4) \cdot 10^{-9}\text{ A cm/W}$  (Ref. 4),

for  $\text{Bi}_{12}\text{TiO}_{20}$ ,  $K_{14} \approx 4 \times 10^{-9}\text{ A cm/W}$  (Ref. 4) and

$K_{14} \approx 2 \times 10^{-10}\text{ A cm/W}$  (Ref. 5).

The reason why  $K_{14}$  is slightly lower for the film than for the  $\text{Bi}_{12}\text{GeO}_{20}$  single crystal may be textural imperfections, i.e., a misorientation of the crystal grains. Another possibility is the presence of an absorbing impurity which does not participate in the generation of the photovoltaic current. This effect is apparently responsible for the discrepancy between the results of Refs. 4 and 5 for  $\text{Bi}_{12}\text{TiO}_{20}$  crystals grown by different methods.

It should be noted that, in contrast with the case of single crystals, in which it is necessary to either lower the temperature or to use a modulation method (at room temperature) in order to observe the effect, which is masked by the contact photo-emf, the Dember voltage, and the photoconductivity, in the case of thin films the photovol-

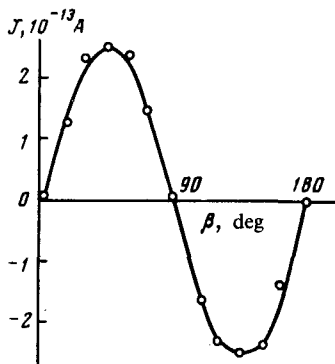


FIG. 2. Orientation dependence of the photovoltaic current in a  $\text{Bi}_{12}\text{GeO}_{20}$  film.

taic current can easily be measured, since it is higher than the contact-photo-emf current. The reason is that the photovoltaic current does not depend on the carrier lifetime,<sup>1</sup> and since the lifetime of the nonequilibrium carriers in textured films is much shorter than in single crystals the contact photo-emf is relatively much less important in films than in single crystals. To estimate the lifetime, we used a pulsed method (we used an LGI-21 pulsed laser with  $t_{\text{pulse}} = 10^{-8}$  s and an S8-12 storage oscilloscope). The lifetime in the films did not exceed  $10^{-6}$  s, while in single crystals it reaches  $10^{-4}$ – $10^{-5}$  s.

From these experimental results we can draw some conclusions. The polarization dependence of the effect is evidence that it is of a photovoltaic nature (an anomalous photovoltaic effect may occur in textured films because of the summation of the photo-emf's of the various  $p$ - $n$  junctions<sup>6</sup>). The observation of the effect confirms the x-ray data, which show that the crystal structure of these films lacks an inversion center, in which case there is typically a piezoelectric effect. Finally, the polarization dependence of the photocurrent can be exploited to determine the azimuthal direction of the crystallographic axes in the texture.

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<sup>6</sup>J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Englewood Cliffs, N.J., 1971.

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