

# Kinetics of photocrystallization and Raman scattering in the bulk amorphous semiconductor GaSb

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A photocrystallization of the bulk amorphous semiconductor  $\alpha$ -GaSb has been detected on the basis of the Raman spectra. The threshold densities have been determined. The behavior of the photocrystallization as a function of the illumination time and the length of the exciting pulses has been studied.

Amorphous semiconductors have a metastable structure, and mechanical, thermal, or optical agents can cause them to undergo an irreversible phase transition to a crystalline state.<sup>1,2</sup> This capability might find applications in data storage.<sup>3</sup> Amorphous semiconductors are usually synthesized as thin films by one of the various

methods used to deposit atoms on a substrate. In the present letter we report the first study of the crystallization kinetics during the application of light to a bulk amorphous semiconductor, *a*-GaSb, prepared by quenching a melted GaSb crystal under pressure.<sup>4</sup> We studied the crystallization kinetics by measuring the Raman scattering spectra.

The Raman scattering was excited by lines of an Ar-Kr laser with a power of 8–130 mW, with focusing to a spot with  $S \approx 4 \times 10^3 \mu\text{m}^2$ . The Raman spectra were recorded with a triple multichannel spectrometer.<sup>5</sup> During pulsed excitation, the length of the pulses was varied from 0.5 to 2 ms (the pulse frequency was 50–200 Hz, and the reciprocal of the duty factor was  $\sim 10$ ), with the help of rotating sector light choppers. Our study was carried out with *p*-polarized exciting light in a grazing-incidence geometry.

When the power density of the exciting light is  $I_0 < 10 \mu\text{W}/\mu\text{m}^2$ , the Raman spectra of bulk *a*-GaSb exhibits—in contrast with the Raman spectrum of an amorphous GaSb film<sup>6</sup>—three bands, at 52, 158, and 226  $\text{cm}^{-1}$  [Fig. 1(a)]. The frequencies of these bands are close to the maxima of the density of vibrational states of the crystal,<sup>7</sup> *c*-GaSb. The most intense band, at 52  $\text{cm}^{-1}$ , which corresponds to the TA density of vibrational states,<sup>7</sup> was not observed in Refs. 4 and 5. This band is forbidden in the Raman spectra of *c*-GaSb by the selection rules, and its intensity in the spectrum

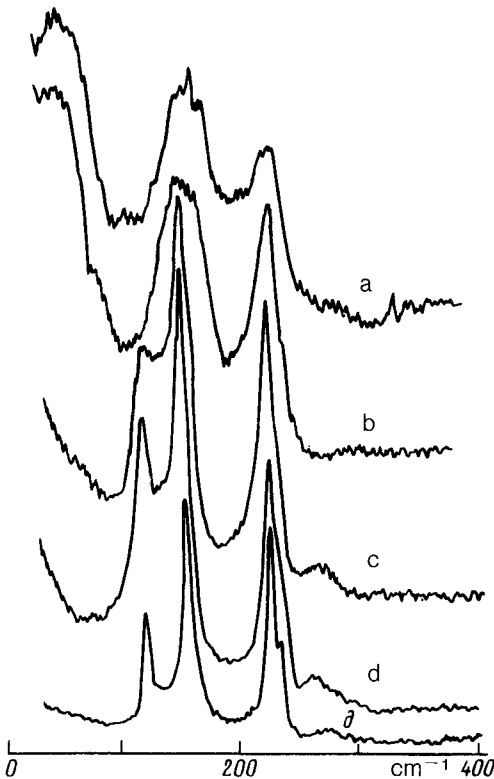


FIG. 1. Raman spectra of *a*-GaSb at 150 K for various power densities of the continuous exciting light ( $\mu\text{W}/\mu\text{m}^2$ ): a—2; b—7.5; c—15; d—25 ( $\lambda_i = 5145 \text{ \AA}$ ). Spectrum e was recorded at  $2 \mu\text{W}/\mu\text{m}^2$  after illumination at a power density of  $25 \mu\text{W}/\mu\text{m}^2$  for 10 min.

of *a*-GaSb is a measure of the extent to which the semiconductor is amorphous. As was shown previously,<sup>8</sup> bulk *a*-GaSb contains inclusions of amorphous antimony, whose spectrum<sup>9</sup> is superimposed on that of *a*-GaSb. The *a*-Sb component is manifested as a slightly higher intensity of the band at 158 cm<sup>-1</sup> than would be expected for *a*-GaSb (Ref. 6). This suggestion was supported by the results of a study of the crystallization of the sample.

At a higher power density,  $I_0 > 10 \mu\text{W}/\mu\text{m}^2$ , the Raman spectrum changes radically (Fig. 1): The band at 52 cm<sup>-1</sup> disappears quickly, and the broad band at 158 cm<sup>-1</sup> is replaced by a doublet 116–153 cm<sup>-1</sup>. The band at 226 cm<sup>-1</sup> is replaced by a doublet 227–233 cm<sup>-1</sup>. The second doublet coincides with the TO and LO frequencies of *c*-GaSb (Ref. 7). The frequencies of the first doublet are approximately the same as those of crystalline antimony.<sup>10</sup> It can thus be concluded from the Raman spectra that the (GaSb + Sb) sample undergoes crystallization at power densities  $I_0 > 10 \mu\text{W}/\mu\text{m}^2$ .

The sample which we studied crystallized when heated above 410 K (Ref. 4). According to our measurements, the threshold densities  $I_0$  for photocrystallization do not change as the temperature is lowered from 300 K to 150 K. Heating the sample to 380 K in an oven causes essentially no change in the shape of the spectrum at  $I_0 = 7.5 \mu\text{W}/\mu\text{m}^2$ . According to our estimates, the temperature of the sample increases linearly during the application of the laser light, at a rate of  $1 \pm 0.5 \text{ deg}/(\mu\text{W} \cdot \mu\text{m}^2)$ . This result agrees qualitatively with measurements of the laser heating of other strongly absorbing materials,<sup>11</sup> and it is evidence that the sample is heated no more than 50–60° at the maximum value of  $I_0$ .

Since the intensity of the exciting light falls off exponentially with a distance into the *a*-GaSb sample, it might be suggested that the photocrystallization begins at the surface of the sample. In this case the fraction (*d*) of the material which has gone into

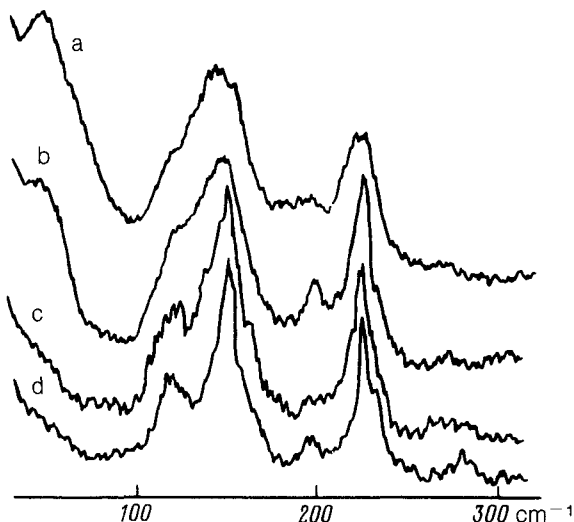


FIG. 2. Raman spectra of *a*-GaSb at 300 K and  $I_0 = 7.5 \mu\text{W}/\mu\text{m}^2$  after illumination for various times: a—10 min; b—1 h; c—2 h; d—4 h ( $\lambda_i = 5145 \text{ \AA}$ ).

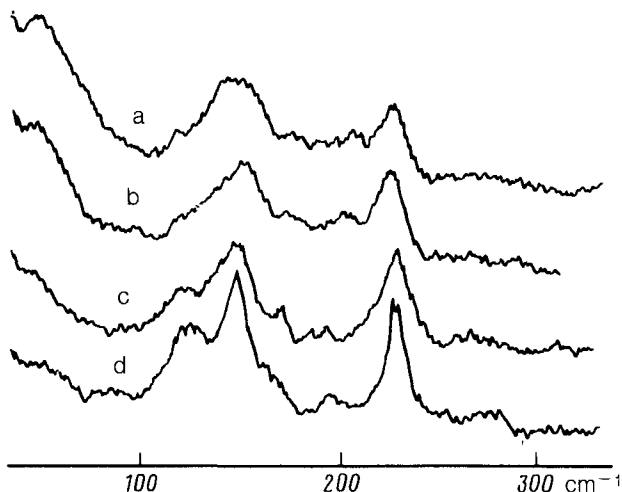


FIG. 3. Raman spectra of *a*-GaSb at 300 K and  $I_0 = 32 \mu\text{W}/\mu\text{m}^2$  for various lengths of the exciting light pulses (in ms): a—0.5; b—1; c—1.5; d—2 ( $\lambda_i = 5145 \text{ \AA}$ ). In all cases the average power was approximately 13 mW.

the crystalline state over a time  $t$  can be estimated from<sup>12</sup>

$$d = 1 - \exp(-Kt), \quad (1)$$

where the constant  $K$  depends on the parameters of the crystallization process (including the power density  $I_0$ ). According to (1), if  $I_0$  is fixed, then the fraction of crystalline phase should increase with the time; this conclusion is supported by the experimental results (Fig. 2). It follows from the time dependence (Fig. 2) that the interface moves at a relatively low velocity. In this case one might expect that photocrystallization would not occur if the pulse length  $t_0$  during pulsed excitation were sufficiently short, even if the power density  $I_0$  were at a level such that crystallization would definitely occur in the case of continuous excitation ( $I_0 > 10 \mu\text{W}/\mu\text{m}^2$ ).

An experiment of this sort was carried out at a comparatively high power density,  $I_0 = 32 \mu\text{W}/\mu\text{m}^2$ , which in the case of continuous illumination causes complete crystallization over a time substantially shorter than the time required to record the Raman spectrum ( $\sim 1$  min). During pulsed excitation with  $t_0 < 1$  ms, we observe essentially no photocrystallization in the Raman spectra (Fig. 3). Such long photocrystallization times ( $\sim 1$  ms) are not surprising since the process by which an amorphous material crystallizes requires the displacement of atoms over significant distances in order to form an ordered structure.

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Translated by Dave Parsons