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Effect of annealing on the optical quality of $AgGaS_2$ and $AgGaSe_2$ single crystals

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Single crystals of $AgGaS_2$ and $AgGaSe_2$ were grown by a modified Bridgman–Stockbarger technique. Pieces of sizes 10 mm × 6 mm × 4 mm and 11 mm × 6 mm × 5 mm of $AgGaS_2$ and $AgGaSe_2$ free from lamellar twins, were cut from the crystals for detailed investigations. The results of infrared transmittance and absorbance measurements indicate that the optical quality of the annealed crystals was much better than that of the as-grown crystals. Experiments on thermal etching were also carried out to study the microscopic defects in the crystals.

1. Introduction

Silver gallium sulphide and selenide belong to the $A^{I}B^{III}C_2^{VI}$ class of semiconductors and are the ternary analogues of such binary semiconductors as ZnS, CdSe, CdS and CdTe. These compounds belong to the 42 m point group symmetry and are therefore birefringent. Both $AgGaS_2$ and $AgGaSe_2$ are important infrared nonlinear optical materials, with the band-gaps of 2.75 and 1.82 eV. respectively. $AgGaSe_2$ is nearly opaque in the visible region but transparent in the infrared range to 0.7 to 20 μm. It transmits very weakly under intense illumination at the far red end of the spectrum. $AgGaS_2$ is transparent in the visible and infrared range from the 0.7 to 12 μm.

Since the beginning of the early nineteen seventies, attempts [1–3] have been made to grow single crystals and study the optical properties of these ternary compounds. In general the crystals exhibit poor optical quality due to the presence of precipitates and compositional variation during the crystal growth. In fact, polycrystalline and nonstoichiometric regions have been observed even in crystals grown from parent components of 99.9999% purity. Traces of oxygen form oxide-rich deposits, which are hard to remove from these compounds.

In recent experiments on transparent materials like succinonitrile Glicksman and co-workers [4] have shown that even very low concentrations of gaseous impurities change the mode of crystallization, convection in the melt, anisotropy, coarsening of the grains and variations in solute diffusion through the crystal lattices. Sometimes these gases are also the cause of voids in the crystals.

Route *et al.* [5] claimed that quenching the ternary chalcogenide crystals from temperatures just below the melting points eliminates the precipitates and enhances the transparency of the crystals. Significant changes in the optical qualities were also reported by annealing the crystals Ag_2S and Ag_2Se. Inspite of some improvement in the optical quality of the crystals, cracking was frequently observed during both the annealing and the quenching processes.

In the present article we report on the optical quality of $AgGaSe_2$ and $AgGaS_2$ crystals which were grown under carefully controlled thermal conditions in a modified Bridgman–Stockbarger furnace. The effects of annealing on the optical qualities are studied in detail. We have also carried out experiments on thermal etching, to study the microscopic defects in the crystals.

2. Experimental details

2.1. Crystal growth

Single crystals were grown in a modified Bridgman–Stockbarger furnace. The adiabatic zone was quite long and one more furnace was placed below the upper furnace. The original charges were rich in selenium or sulphur by 1% with respect to stoichiometric composition. The details of the preparation of mixtures and crystal growth are given by Hopkins *et al.* [6]. The materials used were of the 99.9999% purity and the growth rate was 1 cm day^{-1}.

2.2. Annealing procedure

Pieces of $AgGaS_2$ and $AgGaSe_2$ of the size 10 mm × 6 mm × 4 mm and 11 mm × 6 mm × 5 mm were cut from the as-grown crystals for heat treatment. Each sample was surrounded by a powder of the same composition and annealed in a sealed quartz tube heated for 40 h at 725° C. Subsequently each sample was annealed in vacuum for 48 h.

2.3. Characterization

Crystal characterization was carried out by electron spectroscopy for chemical analysis (ESCA) and optical transmission microscopy. Absorbance was determined using a Beckman spectrophotometer on 5 and 4 mm thick samples of $AgGaSe_2$ and $AgGaS_2$, respectively. Lattice constants of each material were measured by X-ray diffractometry used monochromatized Cu$K\alpha$ radiation and a Philips APD 3600 automated diffractometer.

3. Growth results and the optical quality of the crystals

3.1. $AgGaS_2$

The improved Bridgman–Stockbarger furnace enabled us to grow crack-free single crystal boules

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TABLE I Lattice parameters for the $AgGaS_2$ crystal

Yellow crystal			Dark yellow crystal		
c(nm)	a(nm)	2-c/a	c(nm)	a(nm)	2-c/a
1.030 72	0.575 78	0.2099	1.030 65	0.575 80	0.2101
1.0305*	0.5757*	+0.210			

*See Reference [1].

TABLE II Lattice parameters for the $AgGaSe_2$ crystal

c(nm)	a(nm)	2-c/a
1.088 36	0.598 77	0.1824
1.0886*	0.6992*	0.1832

*See Reference [2].

11 mm in diameter and up to 3.7 cm long. Observations showed that a yellow material crystallized first in the $AgGaS_2$ boules followed by a dark yellow material at the tail of the crystal. The measured lattice constants of both materials are reported in Table I. The results are in good agreement with values reported by Boyd *et al.* [1].

It is very probable that the composition changes during crystal growth but the reason for the compositional change is not fully known at this time. Temperature fluctuations at the growing crystal–liquid interface may cause silver-rich and silver-deficient phases to precipitate with very small difference in their lattice parameters.

The yellow part of the crystal is most transparent to visible light and we chose this part for detailed optical investigation. A small piece, 10 mm, × 6 mm × 4 mm, was taken for the test of transparency; light and dark bands appeared on the crystal faces which may be due to the slip traces or to impurities distributed in the lattice (Fig. 1). Infrared transmission micrography (Fig. 2) shows that the crystal seems to be free from scattering centres. In the longer crystals microcracks were visible similar to those reported by Korczak and Staff [7].

Fig. 3 is a plot of absorbance against wavelength obtained in a spectroscopic arrangement with specially controlled beam geometry. The plot reported here is for a 4 mm thick sample. The minimum value of the absorbance was 1.0 cm^{-1} at a wavelength of λ = 7.5 μm. A loss of this magnitude could be very well due to microcracks and voids which are present in the sample. The data indicate significant bulk absorption in the sample in the short wavelength region. A flat peak at λ = 9.4 μm is due to multiphoton absorption. The absorption coefficient is very comparable to the earlier published results but this value is definitely higher than one would like to have for parametric oscillator applications.

As we have discussed in an earlier paragraph, the as-grown crystals had light and dark bands and scattering centres. After annealing the crystal in its own powder, the dark bands and scattering centres disappeared. Infrared transmission micrographs and micrographs are shown in Figs. 1 and 2 along with the micrographs of as-grown crystals for comparison. Following annealing, the broad band absorption decreased sharply; there was no sign of cracking in the crystal. As shown in Fig. 3, the absorption is greatly reduced across the whole transmission range. The value of α (the absorption coefficient) was much lower for the annealed crystals than that of as-grown crystals. A dramatic effect was the improved uniformity and low α values all over the range. The broad absorption regions between 2 to 6 μm and 8 to 11 μm disappeared and uniform transmission extended up to 12 μm.

3.2 $AgGaSe_2$

The as-grown crystals exhibited a silver-rich phase near the last part to freeze. A 11 mm × 5 mm × 6 mm piece was cut from the crystal for detailed optical investigation; the rest of the crystal was used for the measurements of the lattice constant and other physical properties. The values of the lattice constants are reported in Table II where they are compared with the values reported by Boyd *et al.* [2].

Unlike the $AgGaS_2$ crystal, the selenide crystal was very uniform in colour. The crystal used for the optical evaluation was free from twins and cracks. The overall transparancy of the crystals is illustrated in Fig. 4. A light black band indicates the presence of an optical inhomogeneity like that found in the $AgGaS_2$ crystals. From the infrared transmission micrograph in Fig. 5 we observe various scattering centres in the as-grown

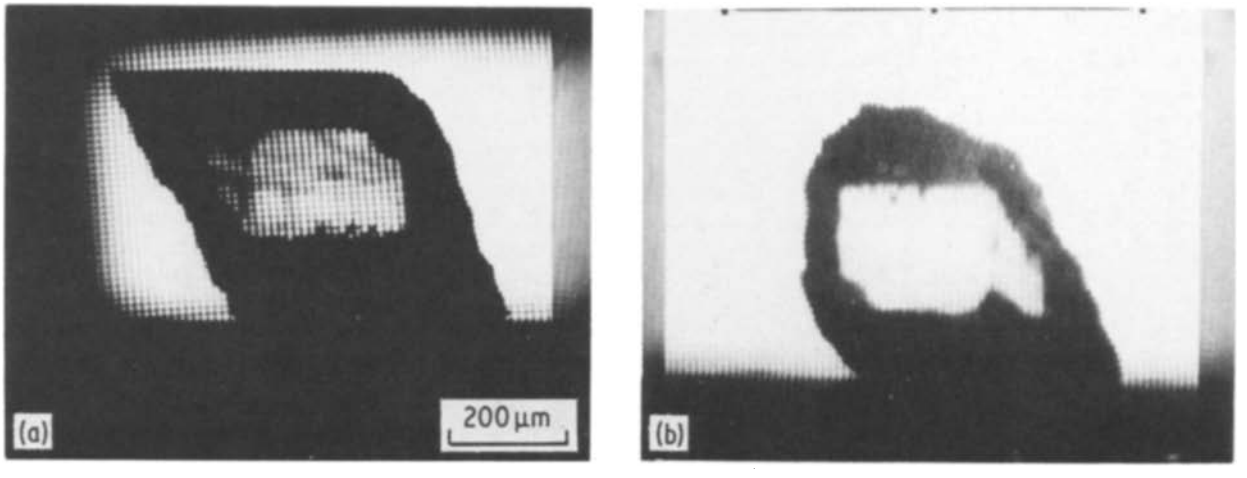

Figure 1 Transparency of $AgGaS_2$ crystals, (a) as-grown crystal and (b) annealed crystal.

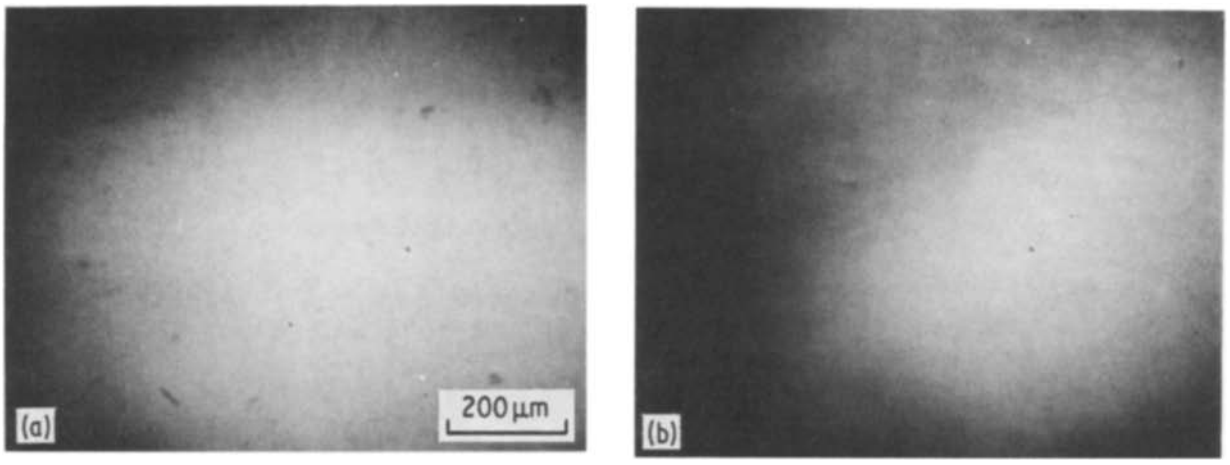

Figure 2 Infrared micrographs of $AgGaS_2$ crystals, (a) as-grown crystal and (b) annealed crystal.

crystals. The exact composition of these dark phases are not known at the present time. We are in the process of analysing the composition of these scattering centres; the results will be reported in later communications.

The results of the absorbance measurements are plotted in Fig. 6 for a 5 mm thick sample. The minimum absorbance in the as-grown crystal was 0.36 cm^{-1} in the region between 4.9 to 7.4 μm. Several peaks of small intensity were observed at 9.1, 13, 13.6, 13.8, 15.3 and 15.9 μm wavelengths, respectively. The intensity and the nonuniformity of the absorption again shows that the scattering is due to optical inhomogeneity. The absorption coefficient is lower than reported values but it is not uniform for the whole transmission range.

Annealing a crystal in its own powder enhanced the transparency and reduced the number of scattering centres abruptly (for example, Figs. 4b and 5b). Breaking up of the bands and the dissolution of the dark black centres were observed as the result of annealing. By comparing Figs. 5a and b it is clear that the bands disappeared first and then the dark black scattering centres started to dissolve. A preliminary analysis showed that these scattering centres are due to compositional variations during the crystal growth and that the centres are silver-deficient phases.

The absorption coefficient measurements for the annealed crystal are shown in Fig. 6 where they are compared with those of the as-grown crystal. The multiphonon peak observed in the as-grown crystal either disappeared or flattened after annealing and the magnitude of the absorption coefficient also diminished. Over the whole transmission range the absorption curve the value of σ showed more uniformity after annealing.

Various authors have reported the annealing of $AgGaS_2$ and $AgGaSe_2$ crystals in vacuum, in Ag_2S or in Ag_2Se at high temperatures. Frequently samples cracked. When both crystals were annealed in vacuum for 40 h it was also observed that they cracked. It made no difference whether the samples were quenched quickly or cooled slowly from the annealing temperature.

4. Thermal etch pits in $AgGaS_2$ and $AgGaSe_2$

Since twinning, cracking and voids have been frequently reported in the literature for these two crystals, it was decided to examine imperfections in the crystals by etch pitting. It was observed that voids are connected with gaseous impurities which are present in the starting components. Examples of micrographs of thermal etch pits are shown in Figs. 7 and 8. Basically the etch pits for $AgGaSe_2$ and $AgGaS_2$ have very similar arrangements. Isosceles triangular etch pits appear on the (1 1 0) surface with a vertex angle of about 65°. This type of etch pit was reported Rinaldi *et al.* [8]. It appears that each of the normals to the longer sides of this kind of pit point into the $(\bar{1}\,\bar{1}\,\bar{1})$

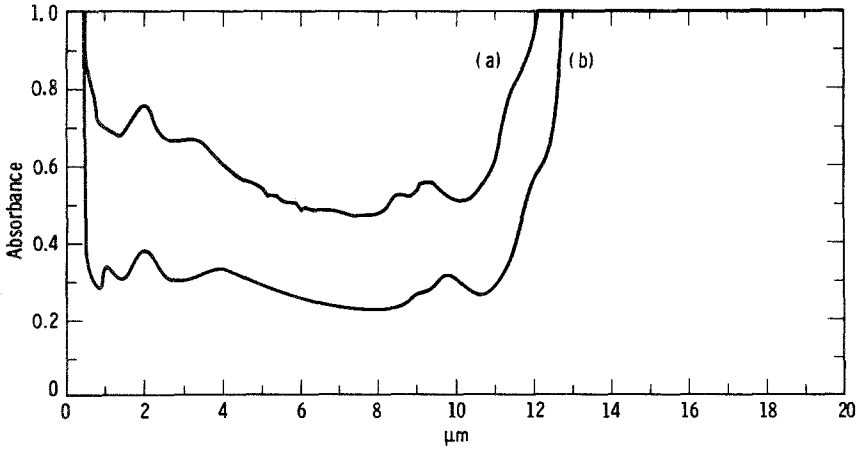

Figure 3 Absorbance spectra for the 4 mm thick crystals, (a) as-grown crystal, (b) annealed crystal.

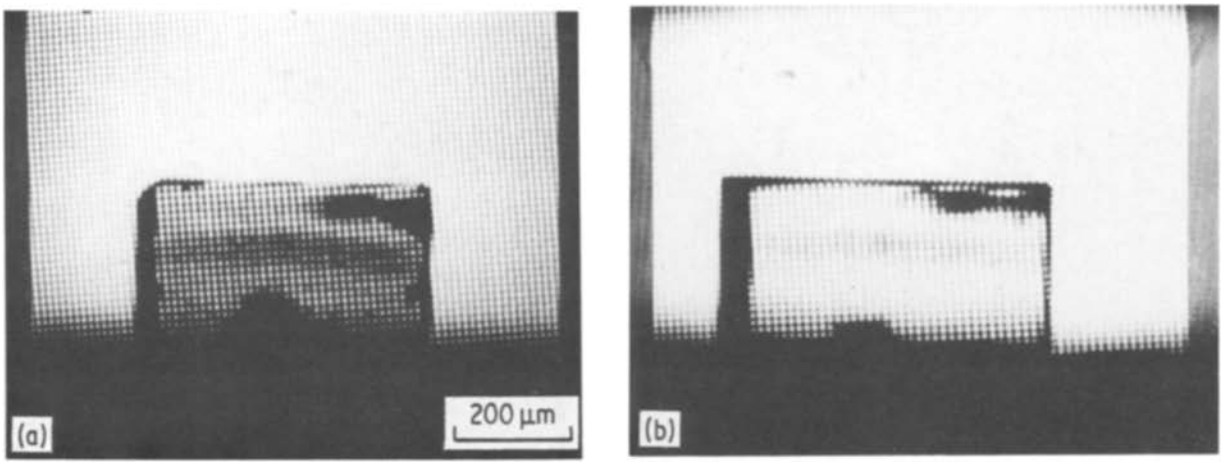

Figure 4 Transparency of the $AgGaSe_2$ crystals, (a) as-grown crystal (b) annealed crystal.

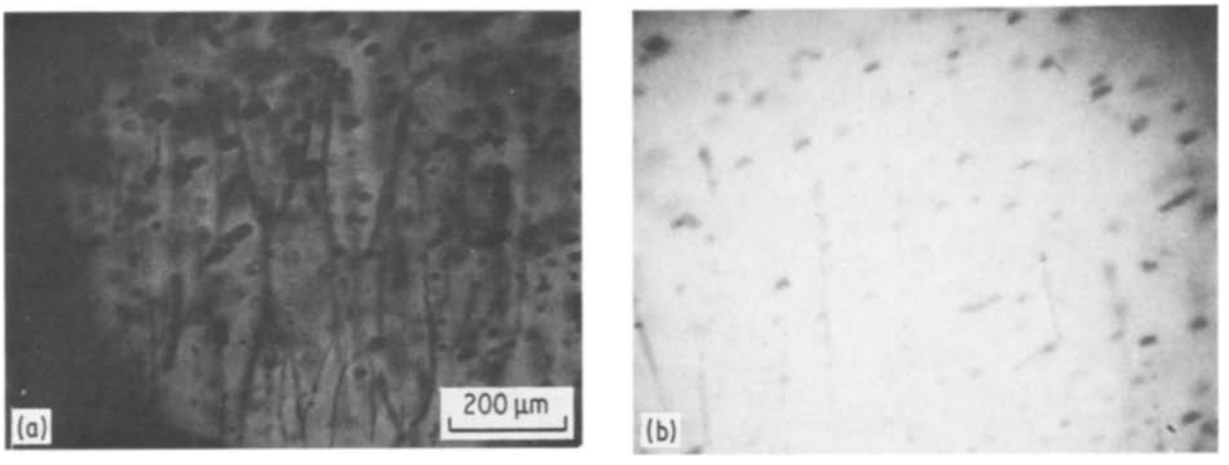

Figure 5 Infrared micrographs of $AgGaSe_2$ crystals, (a) as-grown crystal, (b) annealed crystal.

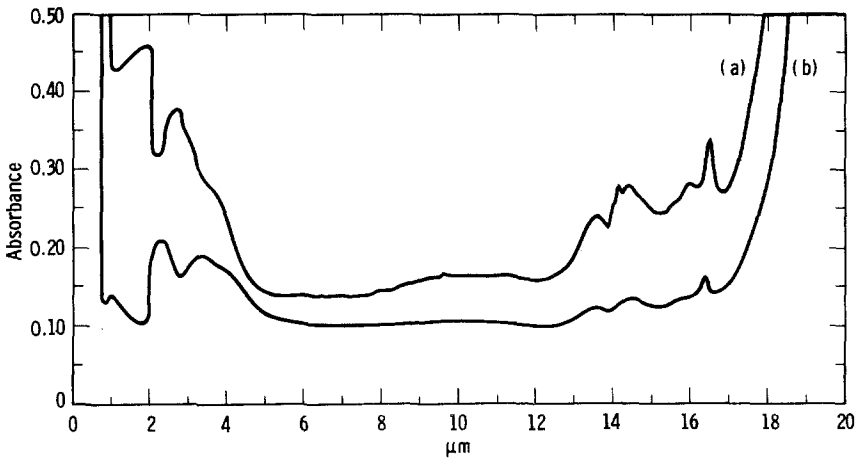

Figure 6 Absorbance spectra for the 5 mm thick $AgGaSe_2$ crystals, (a) as-grown crystal, (b) annealed crystal.

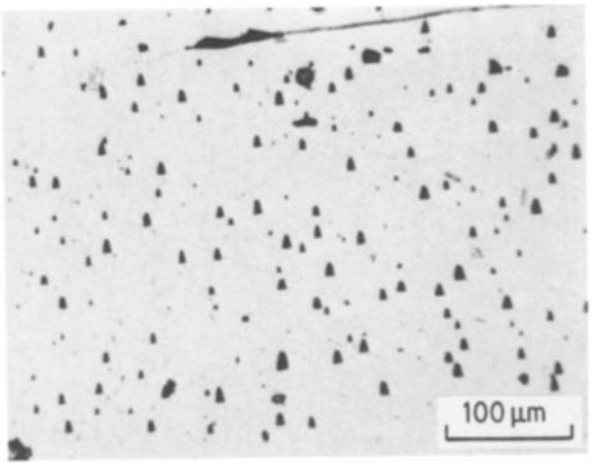

Figure 7 Thermal etch pits in $AgGaS_2$ crystals.

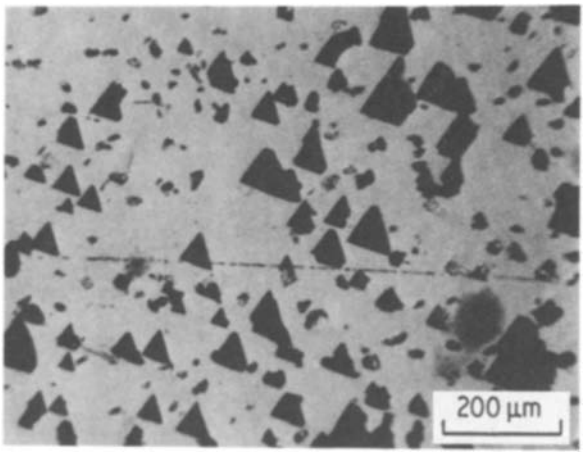

Figure 8 Thermal etch pits in $AgGaSe_2$ crystals.

direction. The shapes of the pits can be explained with reference to Figs. 9a and b. The small triangles are the etch pits on the plane acting as the preferential sites of pyramids appearing as trapezoids. The thermal etch pit densities were 3.9×10^2 and $1.1 \times 10^2 cm^{-2}$ for the $AgGaS_2$ and $AgGaSe_2$, respectively. At the present stage we have not been able to correlate the growth conditions and etch pit density. A preliminary compositional analysis indicates that the etch pits demark silver-deficient phases. Detailed analysis will be published in a later communication.

5. Summary

1. Single crystals of $AgGaS_2$ and $AgGaSe_2$ of the centimetre size have been successfully grown without extensive cracking. Cracking was avoided by modifying the Bridgman–Stockbarger furnace and using two furnaces during the growth.

2. Transparancy of the as-grown crystals were quite good except for a few bands. Infrared transmission micrography indicated a high density of small scattering centres in the as-grown crystals.

3. Annealing the crystals in a powder of their own composition is a very effective method to improve the quality of the crystals. Unlike other annealing or quenching methods, cracking of the crystals is minimized by this technique.

4. The transmittance of both $AgGaSe_2$ and $AgGaS_2$ crystals improved significantly by the annealing technique described.

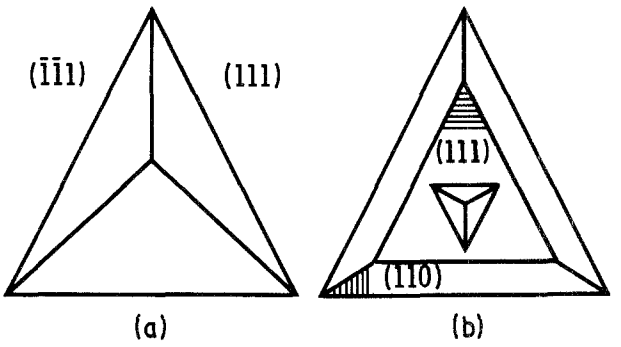

Figure 9 The schematics of (a) triangular (b) trapezoidal etch pit formation.

5. Annealing in a vacuum produces thermal etchpits on both materials. These etchpits are nearly isosceles triangular (vertical angle 65°) which appears as trapezoids on the preferential sites of the pyramid.

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