The Nucleus **48**, No.1 (2011) 61-65

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

GROWTH OF OPTICAL GRADE GERMANIUM CRYSTALS

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(Received October 20, 2010 and accepted in revised form December 31, 2010)

A novel design of Czochralski(CZ) growth station in a low frequency induction furnace is described and growth of optical grade Ge crystal as a test material is performed achieving a flat solid –liquid interface shape. Grown Ge crystals are annealed in air at 450 -500 °C for 4 hrs and then characterized by determination of crystallographic orientation by Laue (back-reflection of X-rays) method, dislocation density studies by etch-pits formation, measuring electrical resistivity by 4-probe technique, conductivity type determination by hot probe method, measurement of hardness on Moh's scale and optical transmission measurement in IR region. The results obtained are compared to those reported in the literature. The use of this growth station for other materials is suggested.

Keywords: *Crystal growth, Czochralski technique, Induction heating, IR Optics, Ge, Optical materials*.

1. Introduction

The semiconducting and optical properties of Ge are of special interest [1,2]. In the production of large Ge casting doped for infrared optics use, one has difficulty in obtaining reproducible high transmittance because of variation in resistivity and polycrystallinity which has been eliminated by growing large diameter Ge single crystals for commercial use [3,4]. Resistive and rf induction heating are the dominant heating methods employed in production of Ge crystals. Thermal design of the system needs to be carefully considered. Using an industrial standard 450 kHz frequency generator the skin depth of the coupling into a graphite crucible / susceptor at 1400 °C is only 2.3mm so that there is no penetration of the field through the crucible into the melt [5] . The heating depth at 10 kHz frequency is about 7 times greater than at 500 kHz [6]. At low frequency (2.5 kHz) the field penetrates through the crucible into the melt producing melt surface oscillations (highly turbulent liquid convection unsuitable for growth) in the conducting melt.

The objective of the present work was to grow Ge crystals for infrared optics use in a system equipped with low frequency generator. For this purpose TDL- J40 crystal growth furnace (Shanghai Institute of Optics and Fine Mechanics, P.R. China) is used. The main features of this furnace are as follows.

i. Heating is provided by 2.5 kHz generator with a variable output to 35 KW.
ii. This system has CZ attachment for crystal growth in vacuum as well as inert atmosphere.
iii. Operating temperature upto 2150 °C.
iv. The furnace was designed at a time 1992/93 for growth of high temperature oxide laser single crystals. A fast response of the furnace allows rapid thermal adjustments to be made during growth. Thus a fairly constant diameter of the cylindrical ingot could be maintained by making rapid adjustment of power as soon as any change in the diameter of the growing ingot is observed. Once sufficient general experience is gained from the operation of this furnace, the production of identical crystals might well be undertaken.

2. Experimental

Fig. 1 shows the growth station designed for pulling Ge crystals. In this station thermally insulated tungsten crucible with an aspect ratio of 2.0 is used as a heat source. A thermally insulated graphite crucible supported by a ZrO_2 tube is placed above the tungsten crucible at a distance of 35 mm. The graphite crucible is heated by radiations from the inductively heated tungsten

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crucible. A Ge seed crystal having [111] orientation with 6 mm diameter mounted in a Pt-Rh seed holder is used. The growth was performed in vacuum ~10^{-5}mbar. The raw Ge material used was supplied by Novotech, Inc. U.S.A. A crucible with 50 mm internal height and 140 mm diameter was fabricated from graphite supplied by LE Carbone Lorraine France. Ge charge in the form of lumps was cleaned with CP4 etchant (3 parts HF,5 parts HNO_3, 3 parts CH_3COOH, 1 part Br_2) and rinsed thoroughly with distilled water. The mass of Ge charge loaded in the graphite crucible was 1820 gm. The crystal rotation and pull rates were 15-19 RPM and 10-20 mm/hr respectively. Crystals were grown by controlling the temperature manually. Grown crystals are annealed in air at 450 – 500 °C temperature range in a muffle furnace.

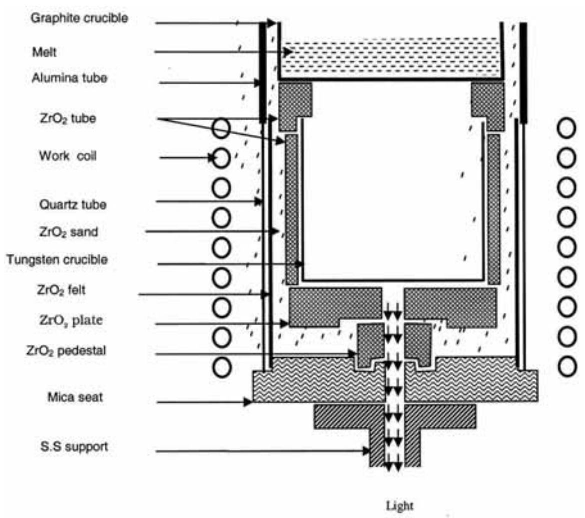

Figure 1. Schematic diagram of crystal growth station for Ge crystals

The crystal shown in Fig. 3 was selected for characterization. The grown crystal was wafered perpendicular to the growth axis to a sample thickness of 3-5 mm with diamond impregnated saw cutting blade. The samples were ground with silicon carbide powder down to 600 grit to produce uniformly rough surfaces which were further polished chemically and mechanically for determination of dislocation density and optical transmission respectively.

The laue pictures [7] were taken from the top and bottom surfaces of the grown crystal to determine the orientation and crystallinity of crystal. Dislocation density was studied in various regions of grown crystals. For this purpose the ground samples were chemically polished with HF: HNO_3 (1:3) at 25 °C and washed thoroughly with distilled water. The etch-pits on the polished surfaces were formed by putting the samples in Ferricyanide etchant (6KOH, $4FeK_3$ $(CN)_6$, 50ml H_2O) at a temperature of 100 °C for 3 min and then washed with distilled water. In order to study the variation of resistivity and hence impurity distribution in the grown crystal, the resistivity measurements were made by 4-probe technique [8] along lines perpendicular to the growth axis at the interval of 3 mm. The equipment used has four probes made of tungsten carbide with sharp tips and 1mm probe spacing (Model S-301-6 Signatone U.S.A). The conductivity type was determined by hot-probe method. The scratch hardness was measured on Moh's scale [9]. This test was done by hardness pencils supplied by Tricen Ltd. U.K. It uses ten reference minerals attached to metallic sticks. The hardness of a substance is determined by scratching it against the reference mineral. If the reference mineral scratches the substance, then it is of equal hardness or harder than the substance, otherwise it is softer than that substance. On the Moh's scale diamond is ranked 10 and talc is ranked 1. For room temperature optical transmittance measurements, the both faces of ground samples were mechanically polished using 1 µm diamond suspension. The parallelism of the surfaces of a sample was indicated by the uniformity of thickness of the sample measured with micrometer. The thicknesses of the optically polished samples were uniform to within ±0.01 mm over the sample area. The final sample thickness obtained was 3 mm. Optical transmission was taken using Perkin Elmer Spectrum One FTIR Spectrophotometer.

3. Results and Discussion

Fig. 2 is the view of Ge crystal during growth. This picture shows the hexagon growing around the seed as viewed from the glass window of the viewing port. This reflects the growth habit of growing crystal in [111] plane.

Fig. 3 shows the typical Ge crystals grown in the newly designed growth station (Fig.1). Crystals with 70 mm maximum diameter are grown. These are grown with the following considerations in mind:

i. To grow a Ge crystal in a low frequency induction furnace from a small amount of material.

ii. There could be several limitations to the growth of crystals from a small volume of melt caused by relatively non-uniform thermal and mass flow conditions.

Figure 2. View of crystal during growth.

Figure 3. Typical grown Ge single crystal. Max.Dia. =65mm

Fig. 4 shows the back-reflection of X-rays Laue picture of grown crystal. This picture consisting of discrete spots showing that the material in question is indeed crystalline and Laue spots are symmetrically placed having 3-fold symmetry. This reflects the characteristic symmetry of the crystal, namely that the top and bottom surfaces of crystal are (111) faces. Crystal has grown in (111) orientation due to the use of seed crystal of same orientation.

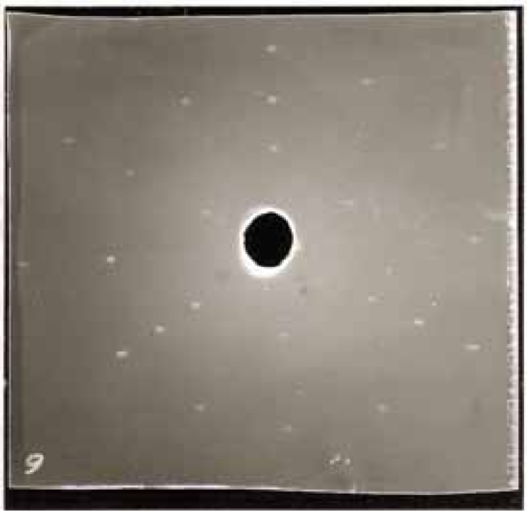

Figure 4. Back reflection of X-rays Laue picture of (111) surface.

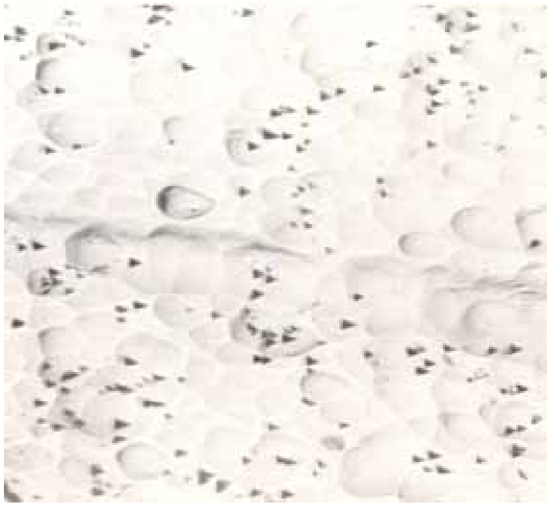

Figure 5. Etch-pits on (111) surface, Magnification 80X.

Fig. 5 shows triangular etch-pits developed on (111) face. The number of dislocations per cm^2 was found by counting the etch-pits. It was found that dislocation densities at the edges and the centre of crystal are $6x10^3$ cm^{-2} and 10^4 cm^{-2} respectively. A possible explanation for the variation in dislocation density is that the dislocations are propagated though the length of the crystal diverging around the growth axis. This would give the maximum density at the axial points with a decrease as one move away from the growth axis. When large crystals are grown, high axial and radial thermal gradients imposed on the growing crystal cause thermal stresses degrading significantly the optical quality of Ge crystals. The thermal stress generates dislocations which can be easily revealed by the appearance of typical etch-pits on the crystal surfaces [10]. The etch-pit density (EPD) of good CZ Ge crystal is usually not less than $5x10^3$ cm^{-2} on the (111) surface plane.

The resulting average radial resistivity measured by 4-probe technique was found to be 10 Ω.cm. All resistivity measurements were reproducible to within ±4% of the average radial resistivity. The radial resistivity variation which is a function of impurity distribution is very uniform as a result of the small radial temperature gradients in the melt due to the special design of growth station. The samples were found to be n-type. The hardness on Moh's scale was found to be 5 which agree with the reported value [11].

Fig. 6 shows the percentage transmission (%T) in the optical wave number 5000 cm^{-1} to 1000 cm^{-1} (2 – 10 µm wavelength) range in a sample of thickness 3 mm with 10 Ω.cm average resistivity. %T in this wavelength range is more than 40% which is comparable to the transmission reported in the literature [12]. Post growth heat treatment (450-500°C for 4 hrs.)which relieves thermal stresses in grown crystal resulted 3 % increase in %T.

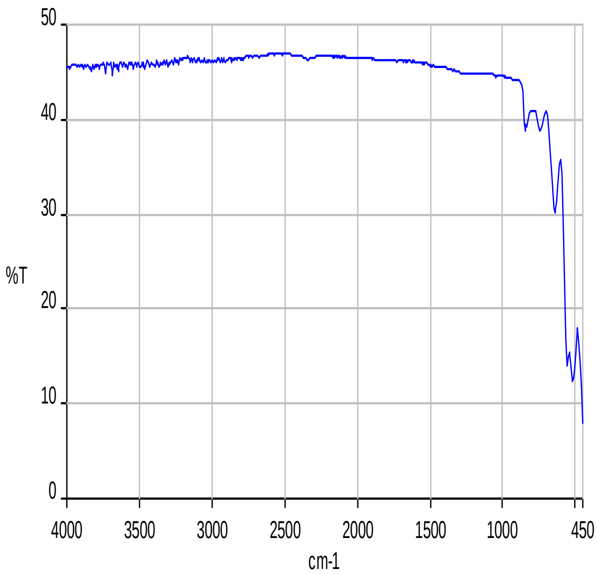

Figure 6. IR Transmission of grown Ge crystal (uncoated). Thickness = 3mm.

4. Conclusions

It is concluded that the crystal pull and rotation rates in the range of 10-20 mm/hr and 15-19 RPM respectively will yield a crystal with diameter in the range of 50-70 mm which is a comfortable diameter to be grown in the newly designed growth station (Fig.1) with a flat solid-liquid interface. The graphite crucible is heated by thermal radiations from an inductively heated tungsten crucible in a furnace equipped with low frequency (2.5 kHz) generator very successfully. Good control over melt temperature is achieved manually. Post growth heat treatment of grown crystal at 450 -500 °C for 4 hrs resulted an increase in %T. This system does not require sophisticated equipment used in the modern CZ pullers and might be of advantage for the growth of crystals of other low melting point materials. The quality of grown crystals is comparable with the ideal grade Ge single crystals with a low dislocation density of the order of| 10^3-10^4 cm^{-2}. Infrared transmission achieved in the grown crystal is comparable to the published literature. From grown crystals optical windows and image forming lenses are fabricated for infrared use in our laboratory. In the subsequent runs crystals of more large and uniform diameter will be grown in this system.

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