ON THE DEVELOPMENT OF CAPILLARY ACTION SHAPING TECHNIQUE FOR GROWING SHAPED CRYSTALS

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Abstract

The equipment used for growing crystals in the form of sheets and tubes by capillary action shaping technique (CAST) under protective atmosphere is described which has been locally designed and fabricated. The growth of LiF crystals in the form of sheets and tubes and Silicon crystals in the form of sheets is described. Si crystals measuring 8 - 10 mm wide, 1 - 1.5 mm thick and 10 - 12 cm long have been grown in the present experiments.

1. INTRODUCTION

Several techniques have been developed to grow crystals in different shapes in the recent years [1-5]. Some of these have been applied to grow Silicon in the form of sheets to avoid the steps of cutting and polishing which not only waste energy and effort but also lead to loss in silicon called Kerf loss. These include the dendritic web process [6-8], the Stepanov technique [9,10], the edge-defined film-fed growth technique (EFG) [3,4,11] which was first applied to silicon by Ciszek [12] and subsequently improved by Ciszek and Schwuttke [13,14] termed capillary action shaping technique (CAST). These new techniques have been applied to the high speed growth of Si sheets, nonagons and tubes [3-5,15]. In this method the liquid is raised to the top of a die by capillary action and crystal growth takes place on top of the die away from the melt surface in the crucible. Crystals can be grown at much higher rates compared to Czochralski (CZ) technique. The shape of growing crystal is determined by the shape of the die top surface. Thus this method is advantageous in producing crystals of required dimensions with controlled dopant concentrations and produces them continuously at high speeds (1-7 cm/min) [10].

In an effort to grow Silicon crystals in the form of sheets we took up the development of the CAST method which has not been attempted in India. The growth of LiF crystals in the form of sheets was tried first [16] and later extended to the growth of LiF tubes and on to Silicon sheets. The growth of LiF in the form of tubes and Si in the form of sheets in a modified vacuum cum atmosphere furnace is reported in the present communication.

2. EXPERIMENTAL DETAILS

The crystal growth furnace is based on the design by Rao and Verma [17] and is schematically given in Fig. 1. It consists of a double walled water cooled stainless steel chamber (6) that can be operated both under vacuum or protective atmosphere. The chamber has four viewing and monitoring ports (12). The lid (5) contains the water cooled pulling tube (4) passing through a vacuum seal (2). The base plate accommodates feed-throughs for power, temperature measurement, gas inlet and outlet and a port for evacuation. Silicon is melted in a graphite crucible (13) heated by a graphite

heater (14) which is fixed to two graphite plates (16) mounted on two water cooled copper electrodes (17) fixed to the base plate with proper insulation. Graphite fiber felt insulation (15) provides necessary thermal insulation. The temperature is measured by a B-type thermocouple placed close to the heater.

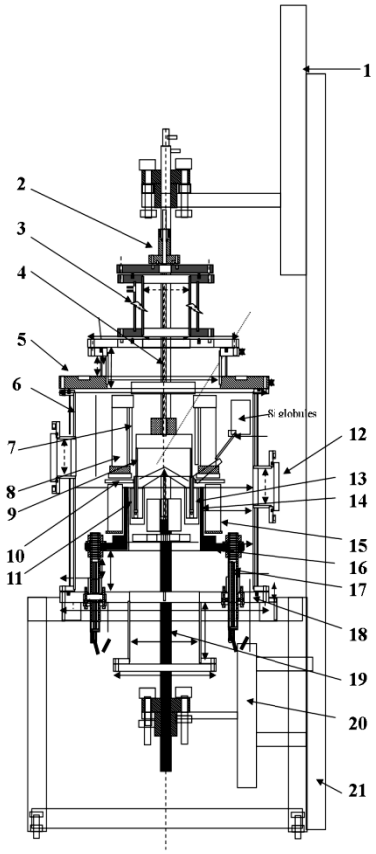

FIG. 1: A schematic of the crystal growing system. (1) Crystal pulling mechanism, (2) vacuum/gas tight seal, (3) intermediate chamber for sheet transfer, (4) water cooled seed pulling tube, (5) water cooled lid, (6) double walled stainless steel chamber, (7) secondary heater, (8) upper radiation shields, (9) growing crystal, (10) die top heater, (11) graphite die, (12) viewing window, (13) graphite crucible, (14) graphite heater, (15) graphite fiber insulation, (16) graphite heater support plate, (17) water cooled copper electrodes, (18) stainless steel water cooled base plate, (19) crucible support and lifting tube, (20) crucible lowering mechanism, (21) furnace mounting stand.

The electrical power to the heater is controlled using a Yokogowa 500P programmable temperature controller coupled to a homemade silicon controlled rectifier (SCR) controller which controls the primary power to a two phase (440 V) to single phase (40 V) transformer. The secondary side (450 A capacity) of the transformer connects to water cooled high purity copper electrodes. Argon gas is circulated around the heater and over the surface of the melt and growing crystal by appropriate inlet and outlet tubes. This provides an inert atmosphere around the growth region in the furnace.

A low voltage and high current power supply is used to prevent sparking between furnace components at low pressures and inert gas atmospheres. Carbon fiber insulation blanket is

used for providing thermal insulation around the graphite heater. The crucible is placed on a support (19) which is fixed to a stainless steel rod that passes through a vacuum seal. The rod could be moved up and down as well as rotated. The seed is fixed to a water cooled stainless steel tube (4) which can be taken in and out through a vacuum seal using the linear motion slide connected to a stepper motor whose speed could be varied from 99 RPM to 1 RPH. The position of the crucible and die with respect to graphite heater is maintained such that lower part of the crucible is held well above the melting point of silicon while top of the die at close the melting point.

The materials for the die and crucible are chosen carefully in the CAST technique based on the considerations such as its wettability with silicon, chemical inertness with the melt and its stability at high temperature [11]. The wetting angle of graphite with molten silicon is 70° and that of silica is 36°. Basic relation that governs the capillary action is,

$$h = \frac{2\gamma \cos\theta}{\rho g r}$$

where h is the height to which the liquid rises in the capillary above the melt surface in the crucible, the surface tension γ of molten silicon is 720 dynes/cm, liquid silicon density ρ is 2.56 gm/cm^3, g is the acceleration due to gravity. For a capillary of 1 mm width, this gives ~ 2.3 cm for h using graphite for the die. Thus the crystal growth is carried out 2.3 cm above the molten liquid surface by the CAST technique which gives the advantage of shaping the resulting crystal and growing at faster rates since the volume of the liquid solidifying above the die top is small. While stainless steel was preferred for the die and graphite for crucible in growing LiF crystals [16], we have used graphite for the die and silica for crucible for melting in case of Si. Since silica softens at the melting point of Silicon (1410°C), a graphite support crucible is used. A silica crucible fitted with a graphite die and filled with silicon powder is placed inside the graphite crucible which is then placed on the crucible support rod in the middle of the graphite heater. Appropriate graphite insulation is placed from the top of the heater and the lid is closed. The furnace chamber is then evacuated to a vacuum better than 0.01 mbar to reduce oxygen partial pressure. The system is then purged with argon gas at a suitable rate. The crucible is heated to the melting point of silicon with the help of the temperature programmer coupled to a homemade SCR power supply to control the temperature within $\pm$1°C as mentioned above. When the temperature is raised above the melting point of silicon (~1410°C) molten silicon rises to the top of the die through capillary action which could be seen from the viewing port. It was found that if argon (Ar) gas is not sufficiently pure the oxygen from the gas reacts with the Si melt and forms (silicon monoxide) SiO layer which prevents the capillary rise. It was also observed that a flow of highly pure Ar gas (< 2 ppm O_2) is needed to maintain the meniscus on the die top.

To initiate crystal growth a thin rectangular graphite sheet was used to make silicon seed crystal plates initially and these Si seed crystals were used in the subsequent growth runs. When the seed is brought into contact with the liquid on the die top, the liquid forms a meniscus between the die top and the seed. The seed plate is pulled up at suitable speed to maintain the crystallization of the melt. After a while the crystal width increases to an equilibrium width. If the pulling rate is too large the crystal detaches and if the rate is too slow the crystal solidifies on the die top. By proper adjustment of the temperature and pull rate the width and thickness of the growing plate could be maintained at a desired value. Plates measuring 1-2 mm thick, 8-12 mm wide and 8-12 cm long have been grown in the present experiments. Efforts are on to increase the width and length while reducing the thickness of the growing crystals by using argon gas jets to cool the growing crystal to increase the growth speed. Theoretical modeling of the thermal system has been performed to obtain the flow rates needed to get stable growth of the sheets [18].

After pulling crystal for the desired length, the growth is terminated by rapidly pulling the crystal away from the die. The furnace is cooled slowly initially up to 1000°C and rapidly thereafter to room temperature. The silicon crystal is taken out from the furnace, cut into samples of appropriate size for testing its properties. The

length and width of the crystal could be increased further by incorporating melt replenishment process. The growth of LiF tubes follows the procedure as described earlier [16] except that the die and seed are in the form of tubes.

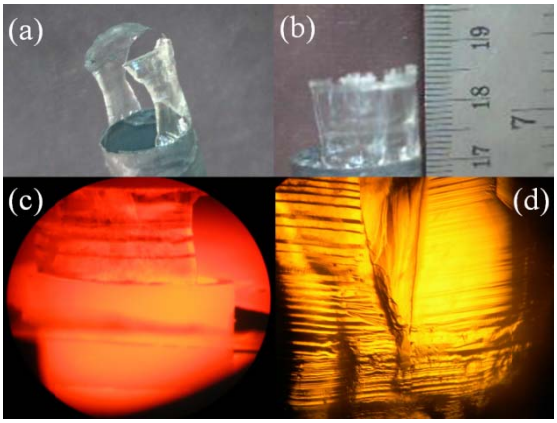

Fig. 2 (a) and (b) as grown tubular LiF crystals, (c) Real time growth view of the LiF tube crystal in the furnace, (d) Growth steps & grain boundaries on the crystal surface seen through an optical microscope

3. RESULTS AND DISCUSSIONS

The grown LiF crystal tubes are shown in the photograph of Fig. 2. Fig. 2 (a) and (b) show partially formed LiF tubes grown at speeds of 1 mm and 0.5 mm per min respectively. Forced cooling of the seed was not used to cool the seed in a controlled manner therefore the growth was slow and uneven. Fig. 2(c) gives the crystal growing on top of the stainless steel die. Fig. 2(d) gives the optical micrograph of the crystal made of 3 grains and the boundary between them. The growth steps are seen as horizontal lines.

The as grown crystals of Si are shown in Fig. 3, coated with an oxide layer due to the formation of SiO. They were cleaned with dilute acid to remove the layer. Viewed under magnification lines are seen parallel to the growth direction indicative of the orientation of the crystal and boundaries are seen indicating several grains. Grains measure 2-4 mm wide and 1-3 cm long in the present experiments. Streaks like lines are seen along the length of the crystal indicating that the crystal grains are growing along the length of the crystal in the pulling direction.

Fig. 3(i) shows a Si crystal plate growing on top of the graphite die. The dark line is the Si liquid meniscus. Fig. 3(ii) shows a Si crystal measuring 1-1.5 mm thick, 12 mm wide and ~10 cm long grown at 1-1.5 mm/min. The insets give the magnified view of the crystal surface (a) three grains are seen with large angle boundaries separating them and (b) the boundary between two crystals with growth striations running parallel to the growth direction. Step like features running perpendicular to the length of the crystal are growth steps caused by the large steps of the stepper motor used in the linear motion system that pulls the crystal upwards. Several crystals have been grown which vary from 8-12 mm width, 10-35 cm length and 0.8-1.5 mm thickness. The crystal appears quite shiny with opaque layer on surface at the upper portions of the growing crystal surface probably due to the (SiO) vapors from the melt. It is well known that oxygen from the silica crucible dissolves in the Si melt and forms SiO. Unless it is flushed from the growth interface it interferes with the crystal growth. If the flushing is not sufficient SiO tends to collect on the cooler upper part of the growing crystal.

Optical micrographs of the silicon crystal grown by CAST technique are given in Fig. 4(a) which shows grain boundaries indicative of multi-crystallinity of the sheets. Lines running along the length of the crystal are growth striations. Fig. 4(b) shows an uneven (top portion) feature which are probably the SiC impurity picked up during pulling the crystal from the reaction of Si with the graphite die top.

These results are a first step towards stable growth of silicon in the form of sheets. We have demonstrated the growth of multicrystalline LiF tubes and silicon plates with good reproducibility. Preliminary electrical measurements on the Si crystals show metallic to semiconducting behavior as these are still not doped during growth. Efforts are on to increase the width and improve the electrical properties needed for photovoltaic applications.

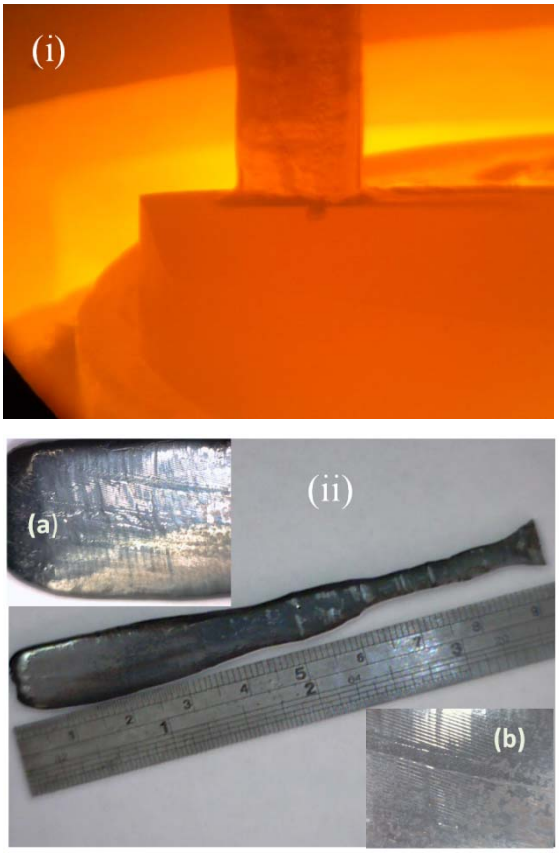

Fig.3 (i) Si crystal growth in progress with the die at the bottom with the meniscus seen as a dark line between the die and the growing crystal and (b) Si crystal measuring 1.5 mm thick, 12 mm wide and ~ 10 cm long; insets gives the magnified view of the crystal showing the growth features (a) 3 grains separated by boundaries the horizontal features are growth striations due to the steps of the pulling system and (b) the boundary of two grains with fine lines running parallel to the growth direction.

4. SUMMARY

The CAST technique has been developed for the growth of various multicrystalline sheets and tubes. LiF tubes and multicrystalline silicon crystal plates have been grown using the CAST equipment. The crystals show growth steps and boundaries indicating multicrystalline nature of the tubes and plates. Optical microscopy reveals the presence of SiC precipitates on the surface of Si crystals. The present quality of the undoped Si crystals is not suited for solar cell applications, even though the efforts are on for making them suitable for this purpose. The development of CAST for Si crystal growth has opened a good potential for producing low cost silicon sheets suitable for photovoltaic applications in the country.

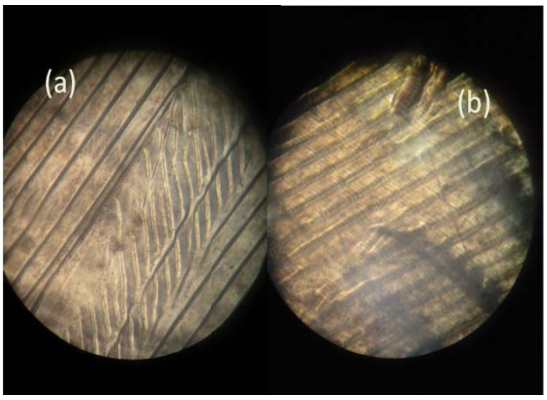

Fig. 4 Optical micrograph of a portion of a Si crystal showing the microscopic features, (a) grain boundary between two grains and (b) SiC precipitates (seen as uneven shaped feature on the growth steps) x 100

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