

Preparation of pure crystalline indium and its characterization

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ABSTRACT

In this study multi-pass zone refining technique was employed to purify indium metal from 3N+ to 5N6 purity level and the refined samples were characterized for their purity and crystalline quality. Major impurities that were targeted for reduction by multi-pass zone-refining include Al, As, Bi, Ca, Mg, Sb, Si, Sn, Ge, Pb, Ga, Cu, Fe, Zn and Ag. The samples were initially homogenized by following a three-cycle melting (heating) and solidification (cooling) scheme. A five pass pre-stage zone-refining experiment(s) of five hours duration on pre-homogenized samples were conducted employing Instrolec 200 zone-refiner. Parameters such as heater temperature, traverse speed, coolant flow and time were optimized. Indium samples obtained from the pre-stage zone-refining process were chemically washed, cleaned and then loaded in the Instrolac PTFE sample tube for final an eight-pass zone refining process. Starting and final stage zone-refined indium samples were characterized by ICP-OES, ICP-MS and XRD. It was found that, the total concentration of impurities reduced from 91.43 ppm to 14.465 ppm after 5 passes and to 4.02 ppm (5N6-99.9996% pure) after 8 passes and the results are discussed.

Key words: Zone-refining, High pure indium, purity analysis.

INTRODUCTION

Indium Phosphide (InP) bulk crystalline wafers and substrates are the technologically important building blocks and platforms upon which InP based ternary, quaternary multi-layered epi-structures are grown. These epi-structures based devices and gadgets find applications in advanced optical communication and strategic areas. Their important and unique micro-optoelectronic, radiation tolerance, hardness, lattice match and material properties make them as potential candidates in the aero-space, defense, and communication sectors. Ultra high pure crystalline grade (7N-99.99999%) indium is one of the primary input materials required for preparing InP compounds based crystals, substrates, epi-structures, as also the indium based MOVPE precursors. InP MMIC and other micro-optoelectronic applications demand 7N pure indium as starting material¹⁻⁴. Zone refining and melting are

the proven process techniques for both purification and preparation of ultra pure single crystals. These techniques play important role in producing ultra high pure crystalline grade metals and alloys. These two processes ensure the driving (segregation) of many of the selected major vulnerable impurities by and large through thermo-physical cum thermo-dynamical activated process to one end of the sample which results in yielding the starting material in a pure and crystalline form⁵⁻¹². In this paper 3N+ indium metal has been purified with reference to select and targeted impurities such as Al, Ga, Cu, Fe, Zn, and Ag and the results are presented.

Zone-refining an outstanding and advantageous process technique for production of micro-opto-electronic grade materials

Zone refining and melting techniques are mainly used for the purification, fractionation of materials. In zone melting or zone refining the

materials to be treated must first be in the solid state. A narrow slice of the material is melted to form a molten zone which is made pass through the entire length of the material. Since the concentration of the impurities in the solid crystallizing from the molten zone is different from that of remaining in the liquid, the impurities or minor components are swept to one end of the column to yield the principal material in a very pure form. By repeating the process several times an ultra-pure product is obtained. Zone-melting or refining introduces fewer impurities during processing. Some common methods of purification actually add more impurities than are removed as the refining as is the case with fractional crystallization. The entire refining process can also be carried out continuously and automatically. Zone refining allows the production of material with a purity of greater than 99.9999% with reasonably pure (4N) starting materials.

Physico and thermo-physical and fractional crystallisation considerations for efficient refining

Instead of a single zone, many molten zones in the sample can be produced and after a single cycle the impurity is concentrated into many bands separated by clear zones of the pure material. The technique of removing the impurity in stages in this way is known as multi-zone refining which enables the purification to be achieved more quickly, than by passing a single molten zone down the entire length of the column. As the molten zone passes down the sample tube the solid crystallizing out behind it is purer than the original material (A) and the impurity (B) becomes concentrated in liquid zone. The purification obtained by zone refining can be defined in terms of the segregation coefficient k , which is the ratio of the concentration of the impurity in the crystallizing solid phase to the concentration of the impurity in the liquid phase. In practice however some of the impurity-rich liquid is occluded in the solidifying substance and this gives a greater value of k than that obtained from the theory, some impurities may be seen trapped amongst the vapor bubbles in the sample. However, with most materials the value of k is less than one and the purity of the material is considerably increased after a single refining cycle. In some cases k is greater than one and the impurity is

concentrated at the beginning of the sample instead of at the end. The factors that are affecting and influencing the refining process include (a) zone travel rate, (b) direction of zone movement, (c) zone size and length of sample (d) diameter of the sample tube, (e) temperature gradient, (f) thermal conductivities of phases, (g) latent heat of fusion, (h) density differences between the solid and liquid, (i) speed of crystal formation, (j) surface tension of the liquid and (k) tendency of the liquid to super cool. In practice efficient refining effect is achieved by using a narrow zone and completing many refining cycles.

Instrument details

The Instrolec 200 refiner available with C-MET, Hyderabad is a special R&D type system having expandable and modular facilities specifically suitable for refining of low melting point materials including indium, gallium and mercury. The system has been further upgraded and automated for handling of samples at 500 gms batch level. The salient features of the instrumentation are detailed below.

Multi-zone operation

The refiner employs the multi-zone refining principle and capable of handling 500 gms quantity of low melting point materials [melting point up to (+) 400 °C and as low as (-) 200 °C]. The instrument has nine separate heaters and eight coolers along the length of the sample tube to produce up to nine narrow molten zones in the material. The sample tube containing the material is moved slowly and reciprocally through the heaters so that the impurities in each separate molten zone are passed eventually into the lower adjacent zone and so towards the end of the tube, as the sample moves through each cycle. In this way the instrument processes the sample more quickly than if a single heater is moved down the entire length of the sample although the final refining effect is the same.

Sample tube

20 mm diameter × 520 mm length teflon sample tube, which can contain up to 500 gms of material (10 mm × 520 mm) with a filling height of 350 mm, was used as the sample tube. Two aluminum guides help to keep the tube in the correct position between the selected two heaters

and coolers as it rests vertically on the drive cam wheel. During refining cycles the tube is made to pass slowly through the heater-cooler assembly.

Heater system

The refiner has nine radiation type electrical heaters, which produce up to nine separate molten zones along the sample tube. The heaters are connected in a series arrangement so that five alternate heaters, series 1 may be operated or 4 alternate heater, series 2, or all nine at once, series 1+2. This combination allows substances, which tend to super-cool to remain in liquid state below the freezing temperature. Each heater is capable of providing a surface temperature of about 400 °C on the sample tube. The temperature of the heaters is controlled by a single control, which gives fine step less regulation. Temperature is calibrated from time to time for each sample with reference to ambient temperature. The temperature control is achieved by regulating it, which causes the sample just to melt. This minimum setting ensures that the molten zone is kept as narrow as possible to give the greatest refining effect.

Cooler System

Between the heaters are eight coolers, which serve to confine the molten zones produced by the heaters. The coolers also help to obtain rapid and good crystallization from the molten zones. Non-corrosive liquid is allowed to flow at a pressure of 175KN m⁻² by using a laboratory chiller. A low temperature coolant (-30°C) is used when the melting temperature of the sample is near to the ambient temperature, so that the molten zones are kept narrow and rapid crystallization occurs.

Drive mechanism

The sample tube is moved vertically at the rate of 25 mm h⁻¹. When the tube has moved upwards through 50 mm i.e. the distance between adjacent heaters, it immediately moves back the same distance. This reciprocating cycle of movement together with the series of heaters has the combined effect of a single heater, a single molten zone, passing down the total length of the sample tube. When a refining cycle is completed, a digital totaling counter on the front panel is actuated. The zone-refiner is shown in fig 1.

EXPERIMENTAL

400 grams of granulated indium (3N+) was subjected to acid washing, cleaning, and etching and analyzed by ICP-OES for its purity confirmation. Sample was heated using hot plate (170°C) and also subjected to gentle stirring for pre homogenization. Then the molten indium was loaded in to the thoroughly cleaned teflon sample tube and cooled down for allowing the sample to solidify. Coolant supply was turned on at a pressure of 175 KNm⁻² and the coolant was allowed to flow through the inlet and outlet pipes of the cooler assembly. The drive mechanism was then started for the first cycle, which runs the tube to pass through the heater cooler assembly of the refiner. The temperature control then changed (rotated) slowly in a clockwise direction to a pre-calibrated position and the solid sample just above the first heater allowed to melt through a stepped regulation procedure (158 to 162°C) with a gradient of 4°C and a 35 mm zone width. After achieving the melting, temperature was regulated to keep the molten zone as narrow as possible during the pre-stage zone-refining.

Cycle counter was set to zero and the drive mechanism started. Experiment continued to complete five refining cycles each of five hours duration. Each completed cycle was recorded on the panel counter. Solidified indium was removed from both ends using the sample extractor. Central portion [band] of the material was again melted and successive final eight pass zoning experiment continued. Typical portion of zone refined samples are shown in fig. 2.

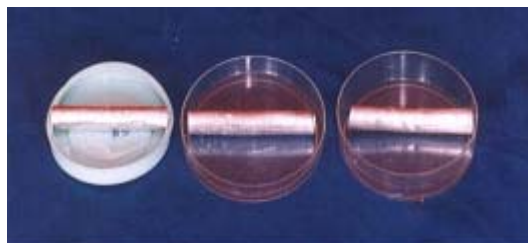
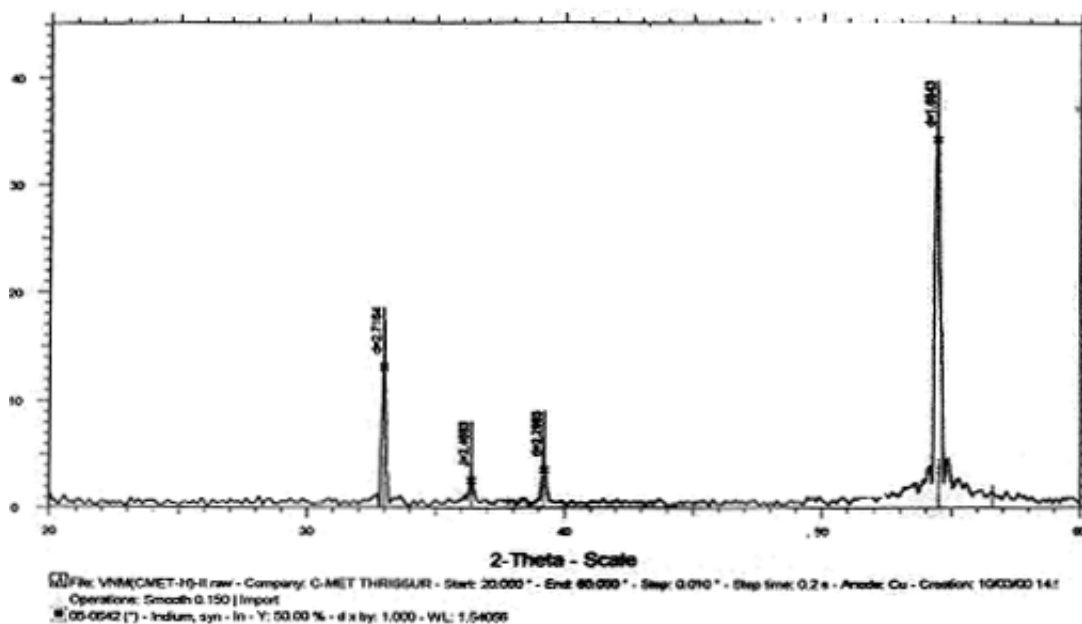
RESULTS AND DISCUSSION

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were employed to estimate the specific targeted impurities such as Al, As, Bi, Ca, Mg, Sb, Si, Sn, Ge, Pb, Ga, Cu, Fe, Zn and Ag. Purity analysis results of starting, pre-refined and zone-refined of indium sample are presented in table 1. The results shows that there is a significant improvement in purity (5N6) in which the total impurity concentration reduced to 4.02 ppm in eight pass zone-refined

Table 1: Analysis of starting and zone refined indium (in ppm)

Element	Starting material ICP-OES	Zone refined (5passes) ICP-OES	Zone refined (8passes) ICP-MS
Ag	1.00	N.D	2.20
Al	2.60	5.54	N.D
As	0.05	N.D	N.D
Bi	3.80	N.D	N.D
Ca	30.00	N.D	N.D
Cu	3.10	N.D	0.66
Fe	5.60	7.15	0.70
Mg	4.20	N.D	N.D
Sb	2.30	N.D	N.D
Si	25.00	N.D	N.D
Sn	9.58	N.D	N.D
Ga	-	0.98	0.40
Zn	-	0.795	0.06
Ge	-	N.D	N.D
Pb	4.20		N.D
Total	91.43	14.465	4.02

N.D: Not detected, -: Not done (limit of detection for ICP-OES -0.1ppm and ICP-MS - 0.01 ppm)

**Fig. 1: Vertical zone refiner****Fig. 2: Zone-refined indium sample****Fig. 3: XRD pattern of multi-pass one-refined indium**

sample compared to 5 pass refined sample in which the impurity concentration reduced to 14.465 ppm with respect to targeted impurities in starting 4N pure indium. However, Ag and Cu impurity show some peculiarity. With increased number of passes the impurities tends to get reduced. Contrary to this Ag and Cu impurity that were not detected after 5 passes were detected to 2.20 and 0.66 ppm respectively after eight passes. This might be due to experimental contamination or accidental redistribution of these impurities instead of segregation. The qualitative trend of impurity (ies) segregation on to the different locations of the rod (ends) was observed. As a preliminary exercise, sampling analysis of zone refined eight pass indium were carried out at different (bottom, middle and top ends) locations of zoned rod, in order to ascertain the segregation trend.

From the interpretation of the results, it was observed that the contamination of the sample took place during the pre, post stage of zone refining and analysis. It was also observed that, the effect of experiment conditions and parameters such as number of passes, zone length, ambient and coolant temperature, environmental cleanliness and over all contamination control aspects both on the pre, post stage zone-refining processes, analysis of indium and mainly the starting material purity plays a crucial role in achieving consistent results.

The crystalline perfection of zone refined 5N+ pure indium sample was also studied by X-ray Diffractometry (XRD) and the results are shown in fig 3. From the experiments and the feed back

available from the results, the following insights were obtained a) carrying out criticality tests so as to sensitize the zone-refiner parameters, experimental conditions during the pre-stage zone-refining is essential, b) standardizing the sample preparation and analysis procedures, effective control of contamination routes helps in further control of impurities thorough modeling the process.

A detailed modeling based on segregation co-efficient versus length of the zone-refined samples to figure out the segregation behavior (concentration profiles and contours) of the Al, Cu, Fe, Ga, Ag, Zn supported by an extensive number of experimentalist trials and insitu analysis for discarding number of impurity bands will provide the experimentalist valuable clues to track and trap the impurities. Further successive multi-pass refining of the pure portion(s) or band (s) [semi-central portions] is required for perfecting the process and achieving repeatable and reproducible results.

CONCLUSION

3N+ pure indium was purified with reference to select and targeted impurities namely Al, Ga, Cu, Fe, Zn and Ag. Zone refined samples were characterized by ICP-OES and ICP-MS and it is confirmed that purity of the zone-refined indium is 5N6 pure with respect to select targeted impurities. Crystalline perfection of the purified 5N pure indium was also studied by XRD and found that material is in crystalline form.

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