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PREPARATION OF TERNARY SEMICONDUCTING COMPOUND $Al_2In_{12}Se_{21}$

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In a search for semiconducting compounds with the energy gaps corresponding to the visible portion of the optical spectrum, we have turned our attention to the ternary compound $Al_2In_{12}Se_{21}$ (Al_2Se_3+6In_2Se_3) in Al-In-Se system. To our knowledge, this potentially prosperous material has not yet been synthetisæd and investigated mainly due two reasons: a)Constituents of the compound have drastically different vapour pressures, so that the problem of very high vapour pressure of selenium appeares at the typical temperatures in common methods of crystal growth, and b) elemental Al reacts with silica (quartz) crucible forming Al_2O_3, so it is necessary to avoid direct contact of aluminum and silica at high temperatures . Development of the new techniques of crystal growth described in earlier publications(1)(2), enables both problems to become solvable: SSD method(3) (synthesis, solute diffusion), used originally for the growth of GaP crystals(3)(1) turned out to be very convinient for a growth of various compounds which constituents have essentialy different vapour pressures. Instead of quartz crucible, "alumina" ones proved to be satisfying for Al compounds.

Firstly, aluminum and indium alloy is produced (purity: Al 6N, In 6N) in a 1:6 ratio by melting it in a high frequ-

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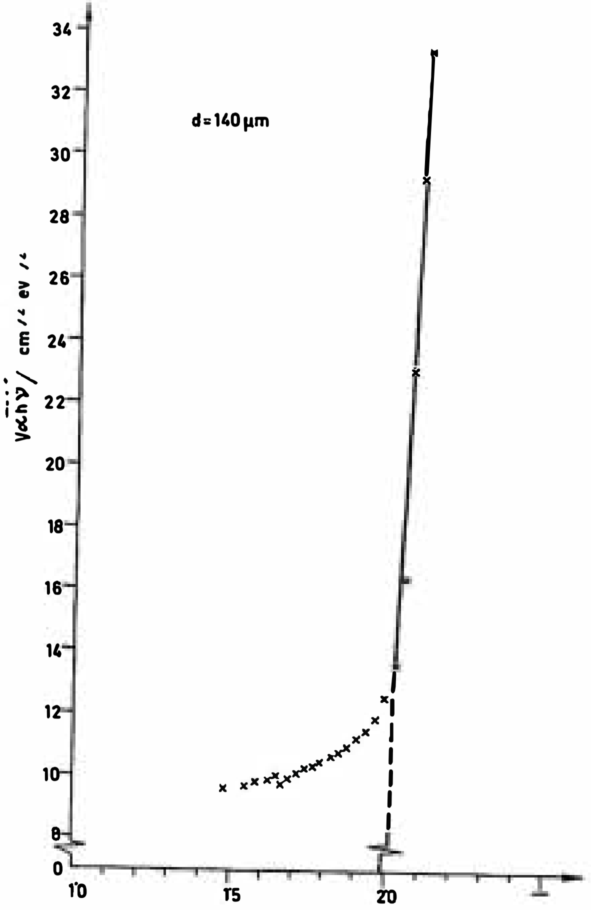
Shematic. diagram of the aparatus for crystal growth, together with its temperature profile, is represented in Fig.1. The "alumina crucible" containing Al-In alloy is placed at the upper part of the reaction vessel, the temperature gradient over it being 50°C/cm. The temperature at the surface of the melt was experimentally chosen to be 1050°C - it has to be lower than the temperature of the melting point of the there-reforming ternary compound. The temperature of the lower part of the evacuated reaction vessel, where the selenium has been placed, was chosen to be 700°C.It coresponds to somewhat more than 1atm Se-vapour pressure for which it was supposed to be high enough to prevent decomposition of $Al_2In_{12}Se_{21}$ crystals. We assume that the crystalisation process goes as follows: Se evaporates in the reaction vessel and reacts with the Al and In at the surface of the melt forming thin film of $Al_2In_{12}Se_{21}$ which then disolves from the lower side of the film and the solute, Se, diffuses into the Al-In melt. The concentration of the solute throughout the volume of Al-In increases depending on time but due to the temperature gradient the solution will reach saturation at the bottom first becouse the temperature is the lowest there. It is expected, therefore that the crystalization first takes place at the bottom of the crucible.

The policrystals thus obtained, were compact, uniform and redish in apearance. X-ray diffraction study has shown that $Al_2In_{12}Se_{21}$ has at room temperature hexagonal structure which corresponds to the high temperature γ- phase of pure In_2Se_3 itself. Similar behaviour was observed for the Ga_2Se_3 - In_2Se_3 systems where the high temperature γ- phase of In_2Se_3 was mainteined all throughout to the room temperature when the per-


d=140 µm
$\sqrt{\alpha h\nu}$ / cm$^{1/2}$ ev$^{1/2}$
34
32
30
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10
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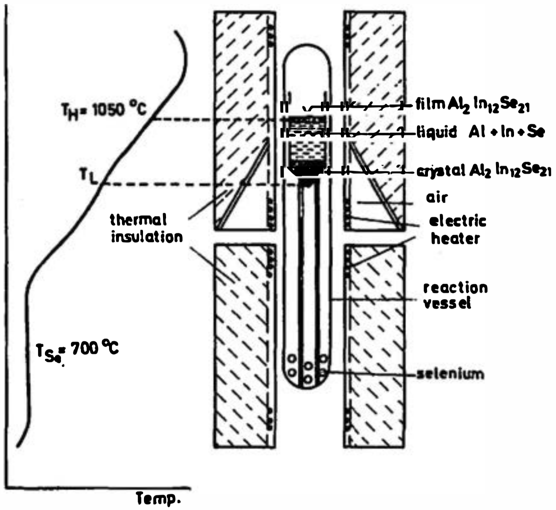
T_H= 1050 °C
T_L
T_{Se}= 700 °C
thermal insulation
film $Al_2In_{12}Se_{21}$
liquid Al + In + Se
crystal $Al_2In_{12}Se_{21}$
air
electric heater
reaction vessel
selenium
Temp.

Fig. 1

centage of Ga_2Se_3 was more than 2% (molar) in the relation to In_2Se_3.

Electrical conductivity measurements have shown very high values for electrical resistivity, somewhat about 10^{11}ohmcm. Samples were quite photosensitive - while exposing them to the source of white light, the resistance drop up to two orders of magnitude was obtained.

The results of the optical measurements are shown at the Fig.2. The abrupt change of the absorption coefficient represents the effect of direct transitions. Due to the insufficiently large grain sizes and therefore significant absorption at the grain boundaries, measured absorption coefficient is, even in the regions of considerable transparency, to high so that we cannot conclude anything positive about indirect transition processes. From $(\alpha h\nu)^2$ versus $h\nu$ representation the width of the forbiden energy gap was calculated, being 2.06eV, corresponding to the wave length of 0.60 um.

The crucial question arise whether crystal is the mixture of two phases Al_2Se_3 and In_2Se_3 crystals or represents only one homogene phase, having the structure of In_2Se_3 in which every seventh In atom is replaced by one Al atom. Up to now, our results confirm this second possibility: beside the X-ray diffraction analysis data and analogy with Ga-In-Se system/4) we can say that our crystal, having forbiden energy gap of 2.06eV and therefore redish in apearance, is entirelly different both from from that of pure Al_2Se_3 (energy gap of 3.1eV, transparent in visible portion of spectar) and of pure In_2Se_3 (energy gap 1.25eV, grey-black in apearance).

In continuation of our work we intend to determine other important mechanical, physical and chemical parameters which would better characterise new compound and to examine changes in electrical properties due to crystal doping with various suitable elements.

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