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METHOD OF PREPARING PURE INDIUM PHOSPHIDE

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This invention relates generally to improved semiconductive materials, and to improved methods of preparing them. More particularly, the invention relates to an improved method for preparing and purifying a semiconductive compound: indium phosphide.

It is well known that semiconductive germanium devices have rather stringent operating temperature limitations. This is due to the relatively small energy gap width of germanium which permits the electrons to be thermally excited from one energy level to another at temperatures not very much higher than room temperature. For this reason other semiconductive materials having greater gap widths, and hence greater thermal stability, have been investigated. One material having a suitable energy gap width is silicon; others are the intermetallic compounds such as aluminum antimonide, gallium arsenide, and indium phosphide, to mention a few.

In an application of the instant inventor and Ronald J. Guire, Serial No. 523,718, filed July 22, 1955, now Patent No. 2,871,100, a method of producing crystalline indium phosphide from a melt is described. As is the case with most semiconductive materials after the initial production of the semiconductive material it is necessary that it be purified to a high degree in order to make the material of practical use in semiconductor devices. A semiconductive material having too large a concentration of impurities therein exhibits very low resistance and therefore fails to function satisfactorily when employed in a device. Most of the known semiconductor materials such as germanium and silicon may be purified to the required degree by a process such as "zone-melting." In this process a small molten zone traverses a long charge of the semiconductive material, in effect sweeping impurities along with it so that most of the impurities are frozen out in the terminal portion of the charge. This process is well known and is described by W. G. Pfann in an article entitled "Principles of Zone Melting" in the Journal of Metals of July 1952, page 747.

The purification of a compound such as indium phosphide by zone melting is accomplished only with difficulty. One of the chief objections to zone-melting indium phosphide is the danger of explosion. This is because the compound decomposes into its constituents prior to melting and must, therefore, be maintained under a vapor pressure of the volatile element (phosphorus). Since it was found that purifying by zone-melting required a large number of passes of the molten zone to achieve significant purification, it is necessary that the material be maintained in a closed container at high temperatures under a phosphorus pressure of several atmospheres for two to three days. In addition to the above-mentioned pressure of phosphorus, the vapor of undissociated InP adds to the total pressure in the container. Added to the danger inherent in zone-melting is the fact that the process is inefficient and time consuming especially in the case of indium phosphide. For example, it was found that it took five passes of the molten zone to reduce the impurity concentration by only a factor of four, that is from an initial impurity

concentration of about 4×10^{17} atoms per cc. to $1.\times10^{17}$ atoms per cc.

It is therefore an object of this invention to provide an improved method for preparing a pure semiconductive intermetallic compound one of whose constituents is volatile.

Another object of the invention is to provide an improved method for preparing pure crystalline indium phosphide.

Another object of the invention is to provide an improved method for preparing crystalline indium phosphide with a relatively high degree of purity.

Still another object of the invention is to provide an improved method for preparing pure crystalline indium phosphide quickly and efficiently.

These and other objects and advantages of the invention are obtained by preparing an initial quantity of indium phosphide under the purest conditions possible and then decomposing that quantity of indium phosphide and thereafter reacting the pure phosphorus vapor obtained, with a new quantity of pure indium.

In practicing the invention the first step is to prepare the compound, indium phosphide, under the purest possible circumstances. The compound is prepared initially according to the method described in the aforementioned co-pending application of Guire and Weiser. Briefly, a quartz tube is provided having relatively thick walls to minimize the danger of explosion. The purest available indium in chunk form, for example, is inserted in the quartz tube at one end thereof. Also within the tube and at the opposite end of the quartz tube is a quantity of phosphorus, again the purest available. After evacuation, the tube is sealed off. The amount of phosphorus is that required to react with the indium in a stoichiometric ratio plus the amount to give a phosphorus vapor pressure at least equal to the dissociation pressure of InP at its melting point, or approximately 2 atmospheres. A typical example is 14 grams of indium and about 4.3 grams of phosphorus for an ampule having a volume of 10 cc.

The end of the tube containing indium is heated to the temperature (1060° C.) to which it readily reacts with the phosphorus. The phosphorus is made to contact the indium by heating it to a temperature of about 400° C. at which the desired reaction vapor pressure is obtained. Upon completion of the reaction, the compound formed is molten and highly unstable, the phosphorus tending to escape from the melt. In order to prevent such escape, the phosphorus end of the tube is heated to further vaporize excess phosphorus to provide the vapor pressure in the tube of about three atmospheres. Thereafter the melt is slowly cooled under a temperature gradient so as to produce solid crystalline indium phosphide. It is not necessary that the initial indium phosphide be gradient-cooled so as to produce it in crystalline form. This is because the initial indium phosphide is to be decomposed so as to provide a pure phosphorus vapor to be reacted with another quantity of indium which second quantity of indium phosphide will be produced in the desired crystalline form. Some advantage in purification may be achieved, however, if the first batch of indium phosphide is gradient-cooled due to the segregation of impurities by the zone melting process.

The impurity concentration per cubic centimeter in the indium phosphide thus produced is too great to be useful in some semiconductor devices such as transistors. For example, one ingot thus prepared had an impurity concentration of 10^{18} atoms per cc.; another ingot had an initial impurity concentration of 3×10^{17} atoms per cc. Since impurity concentrations of much less than about 10^{16} atoms per cc. are desired for most applications, the compound must be further purified. According to the invention, this may be accomplished by placing the indium

phosphide obtained, as described, in another quartz vial at one end thereof. A new and pure quantity of indium is placed in the other end of the ampule. The quantity of indium placed in the vial may be about the same as the first quantity of indium if it is not intended to melt the purer indium phosphide produced so as to achieve crystallization thereof. If the indium phosphide is to be melted and crystallized, it must be done under a phosphorus vapor pressure to prevent the escape of phosphorus from the melt as taught in the above-mentioned co-pending application. In such a case the new quantity of indium will be less than the initial quantity of indium used to make the first batch of indium phosphide. This is because the phosphorus vapor produced by the decomposed indium phosphide must be sufficient to react with all of the indium present and to also provide an excess phosphorus vapor pressure in the vial. Hence, all of the phosphorus vapor released by the decomposition will not be available for reaction. A typical quantity of indium to prepare the second batch is about 10.5 grams for about 15 grams of InP to be decomposed.

After evacuating the vial, the first step is to heat the indium phosphide to approximately 850° C. while maintaining the indium end of the ampule relatively cool (at room temperature for example). The indium phosphide rapidly decomposes and the phosphorus vapor condenses in the cold or indium side of the vial. Upon completion of the decomposition, the ampule is sealed off at a constriction at its center and the portion containing the initial indium phosphide is removed. The vial containing the condensed phosphorus vapor and indium is then heated up to about 900° C. at which temperature the phosphorus reacts with the indium to form a new quantity of indium phosphide. The reaction can be speeded up by employing a temperature of 1060° C. whereat the indium phosphide formed is molten. If it is desired to melt the indium phosphide for crystallization purposes, it must be done under the aforementioned phosphorus vapor pressure. Upon obtaining a melt of the indium phosphide, it may be slowly cooled so as to result in solid crystalline form. This is accomplished by establishing a temperature gradient in the indium phosphide melt by having one end of the melt near the heat source, for example. In practice, it was found that good results were obtained with a gradient of about 100° C. per cm. along the melt and having the coldest end of the melt just at the melting temperature of about 1060° C. The purpose of the gradient is to prevent the freezing due to super cooling of more than just a very small tip at the cold end of the melt, otherwise, a mass of many small crystals results. The preferred rate of crystal growth is 0.5 mm. per hour and this rate is obtained by slowly lowering the overall temperature about 5–6° C. per hour. The frozen mass is composed of large nearly perfect grains of indium phosphide.

The indium phosphide prepared by the method of this invention was found to be purer by whole orders of magnitude than that initially prepared. For example, one ingot having an initial impurity concentration of 10^{18} atoms per cc. was decomposed and yielded, according to the method of the invention, an ingot with an impurity concentration of 2.4×10^{16} atoms per cc. The ingot having an initial impurity concentration of 3×10^{17} atoms per cc. was decomposed and yielded, according to the method of the invention, an ingot with an impurity concentration of 7.5×10^{15} atoms per cc.

There thus has been described a novel method for obtaining crystalline indium phosphide of much greater purity than heretofore obtainable even by the use of time-consuming processes. Furthermore, the method of the invention achieves this purification with a minimum of danger from explosions.

What is claimed is:

1. A method of further purifying relatively impure indium phosphide which has been prepared by vaporizing separate quantities of indium and phosphorus, reacting the vapors to produce said indium phosphide and cooling the reaction product, said method comprising providing a quantity of said relatively impure indium phosphide at one end of an evacuated container, providing at the other end of the container a quantity of relatively pure indium, heating said relatively impure indium phosphide to a temperature sufficient to cause decomposition thereof to yield relatively pure phosphorus vapor, reacting at least some of said relatively pure phosphorus vapor with said relatively pure indium to form a relatively purer compound of indium phosphide, melting said relatively purer compound under a vapor pressure of unreacted phosphorus, establishing a temperature gradient in said molten compound from one end to the other, and recovering relatively pure crystalline indium phosphide by slowly freezing successive portions of said molten compound proceeding from the coldest to the hottest portion thereof.

2. A method according to claim 1 wherein said quantity of relatively pure indium is sufficient to react with only a portion of said relatively pure phosphorus vapor so that there is enough remaining phosphorus vapor to establish a vapor pressure thereof of about three atmospheres.

3. A method according to claim 1 wherein said temperature gradient is about 100° C. per cm.

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