Pure Chemical Elements for Semiconductors

1969

Marshall Sittig

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NOYES DEVELOPMENT CORPORATION
Park Ridge, New Jersey, U.S.A.

Noyes Development, S.A. London, England

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FOREWORD

This Electronics Materials Review presents techniques for producing pure chemical elements for semiconductors and is based on the U.S. patent literature since 1960.

Electronics Materials Reviews are a series of comprehensive up-to-date studies of the technology of production and utilization of the materials used in today's and tomorrow's electronic devices. They represent the basic technology behind investment in such areas as:

- solid state lasers
- magnetic recording media
- thermoelectric devices
- faster, more compact computers
- improved solar cells
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- electroluminescent materials for color television
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- new and exotic batteries

They are written from the practical, processing point of view giving specifics about material characteristics and construction of equipment as well as details of operating conditions. These volumes are of prime interest to managerial, research, engineering development, marketing personnel etc., in the broad range of industries producing and consuming electronic materials. Each Review includes a number of illustrations.

Electronics Materials Reviews are based primarily on the patent literature, supplemented by other commercial information and data to present as complete a picture as possible. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from the patent literature is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

These Reviews are bound in paper in order to close the time gap between the "manuscript" and the "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new material or process and the

granting of a patent but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Marshall Sittig, well known for a wide variety of publications dealing with both inorganic and organic chemical technology, is associated with Princeton University. These Electronics Materials Reviews by Marshall Sittig, save you considerable time, effort and money – he has gathered and selected the pertinent information in the field and presented it in a logical, easy-to-read format.

These Reviews are organized in such a way that the Table of Contents also serves as a subject index. Further, they are indexed by inventor, patent number, and company for the reader's convenience. Thus, they tell you quickly who is doing what today.

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INTRODUCTION

Dating from the discovery of the transistor in 1948 at the Bell Telephone Laboratories there has developed a need for a whole new family of hyperpure materials. Any impurities in these materials are measured in parts per million or even in parts per billion.

The pure chemical elements discussed here may be used in elemental semiconductors — as in the case of silicon or germanium — or they may be components of compound semiconductors as in the case of gallium and arsenic in gallium arsenide, for example.

A group of new processes have been developed for the production of these hyperpure materials involving the reduction of oxides and halides, the disproportionation of halides, the decomposition of metal alkyls, the decomposition of metal hydrides as well as various electrolytic techniques.

Following the various preparative methods listed above, special purification techniques are often used to attain the high purities required. These techniques include distillation, recrystallization, electrolytic refining, chemical treatment and zone refining.

ANTIMONY

Antimony is a Group V element. It combines with several group III elements to form semiconductor compounds. Among these important compounds are indium antimonide, gallium antimonide and aluminum antimonide.

ELECTROLYTIC PROCESS

Les Produits Semi-Conducteurs

A process developed by R. Beau (U.S. Patent 3,108,934; October 29, 1963; assigned to Les Produits Semi-Conducteurs) comprises dissolving antimony oxide, Sb_2O_3, in an electrolyte and electrolytically separating arsenic and antimony from impurities, transforming the antimony to oxide and with the arsenic to trichloride and separating the arsenic from the antimony by distillation, dissolving the antimony trichloride in an electrolyte, and electrolytically separating it from residual impurities. In this process the following steps are carried out in succession.

A first electrolysis in a tartaric medium at low potential which eliminates impurities such as copper and bismuth, a second electrolysis in tartaric medium under a higher potential which produces a deposit of antimony still contaminated by arsenic, the dissolution of the contaminated arsenic and a distillation which first eliminates water and acid and which later eliminates the arsenic, and finally an electrolysis which separates the antimony from the last impurities.

According to the process, antimony of high purity is prepared from commercial antimony oxide, Sb_2O_3, which can be derived from the purchase of oxide or by making the oxide from impure metallic antimony. The oxide is dissolved in an aqueous solution of tartaric acid and the solution obtained is subjected to a low intensity electrolysis, preferably on the order of 0.6 ampere.

The difference in potential should be selected so that copper and bismuth present in the impurities are deposited at the cathode together with a minute quantity of antimony. In practice, the cathode potential may be in the neighborhood of -0.210 volt as measured by comparison with a calomel reference electrode. The solution of antimony in tartaric medium from which the impurities bismuth and copper have been removed is then subjected to a second electrolysis, either by flowing it into a second chamber or by changing the electrodes

in the first chamber, at a higher potential selected so that antimony and arsenic are deposited on the cathode while the other impurities such as iron, tin, zinc, silver, aluminum and nickel remain in the solution. This second electrolysis may be effectuated at a cathode potenial of about -0.32 volt, measured with respect to a calomel electrode, the current being on the order of 6 amperes at the beginning of this step and falling to about 1.2 amperes at the end of this step.

The antimony recovered at the cathode is free of copper and bismuth but it still contains much arsenic as well as some impurities which have been intrained during the deposition of antimony on the cathode. The antimony is removed from the cathode and oxidized, nitric acid being an effective oxidizing agent, producing antimony oxide, Sb_2O_3, insoluble in water. After washing with boiling water the oxide is put in concentrated hydrochloric acid solution which produces arsenic trichloride from the arsenic. This solution is subjected to distillation during which the water-HCl azeotrope is eliminated. The arsenic chloride boils at about 130°C., is partly intrained by the azeotrope, and is distilled itself as the temperature rises being totally eliminated from the residual mass by the time it attains 220°C., the boiling point of antimony trichloride. After this elimination the distillation is stopped. During the course of this distillation it is advisable to have in the boiling mixture a small quantity of high purity antimony in order to prevent the formation of pentavalant antimony.

The antimony trichloride obtained by distillation, free of copper, bismuth and arsenic, is then given a last purification by electrolysis in order to separate the antimony from its last traces of impurity. This electrolysis is effectuated in a medium so chosen that the antimony is not compounded with the solvent medium. It has been found that a particularly appropriate medium for the final electrolysis is a mixture of hydrochloric and sulfuric acids. The sulfuric acid prevents the hydrolysis of antimony chloride which is favored by the high concentration of the solution. The sulfuric acid does not change the properties of the bath, which retains its non-reactive characteristic favorable to the separation of impurities by controlled voltage by electrolysis.

Thus one obtains from this process crystalline, non-explosive antimony of high purity. The final electrolysis is preferably carried out in a solution containing from 10 to 50 grams per liter of antimony under the form of antimony trichloride in the presence of free hydrochloric acid of 1 N to 2 N concentration and of free sulfuric acid of concentration between 1 N and 4 N. During the final electrolysis one prefers to use a solution of antimony trichlorde of 40 grams per liter in a mixture of hydrochloric acid and sulfuric acid 1.5 N and 3.3 N, respectively. With this solution one totally avoids the risk of hydrolysis in the electrolytic baths. The temperature may be maintained favorably around 25° to 30°C. It is advantageous during the final electrolysis to maintain the cathode potential between -180 and -190 millivolts measured as aforesaid. At these potentials the current densities are about 1 to 5 milliamperes per $cm.^2$

The nature of the electrodes used is not critical for the operation of the final electrolysis but it is preferable to use pure antimony cathodes or platinum or tantalum cathodes on which the antimony deposits without forming alloys and from which it is readily detachable. When one uses platinum cathode it is preferable to use a reducing electrolytic bath containing a reducing agent such as hydroxyl-amine in order to prevent the release of pure chlorine capable of attacking the anode. One prefers to use habitually pure graphite anodes, for

example, 99.999% pure, which are not attacked by the bath.

The apparatus as shown in Figure 1 includes a tank 1, a plurality of graphite anodes 2, 3, 4 which are surrounded by glass diaphragms 2a, 3a, 4a which have a portion 2b, 3b, 4b which permits diffusion of the bath. The diffuse part of the diaphragms 2b, etc., may be composed of a plate of fritted glass disposed below the lower ends of the electrodes. The diaphragms 2a, 3a, 4a are sealed at 2c, 3c, 4c to the anodes by plastic joints. The diaphragms have lateral ports 2d, 3d, 4d which allow the escape of the chlorine formed during the electrolysis.

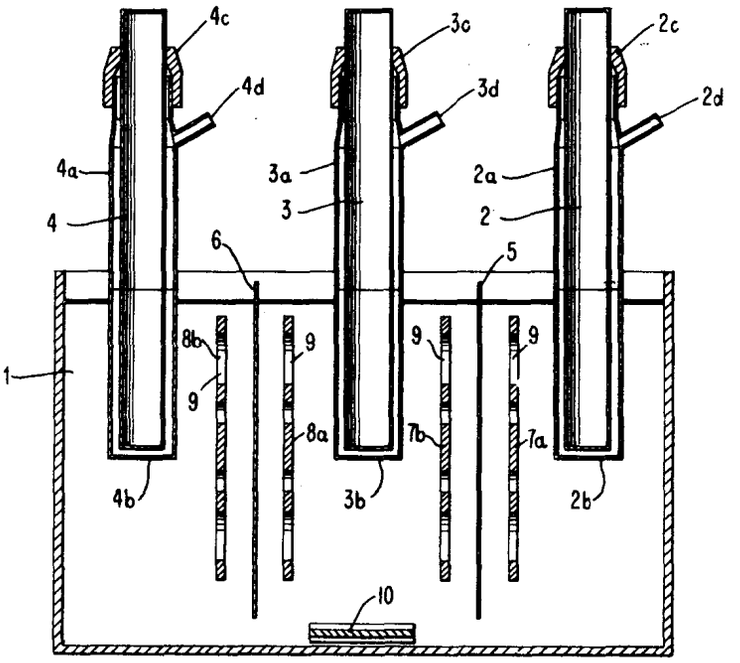
The cathodes such as 5 and 6 are of a classic type, of platinum for instance, and they are isolated from the anode compartments by screens 7a, 7b, 8a, 8b which have apertures 9, of smaller diameter at the center and increasing in size towards the rim. They are advantageously constructed of plastic plates and their centers are located approximately in line with the diffusion plates which lead to the electrodes. In this way equality of current density is assured over the whole surface of the cathodes during the electrolysis and is not concentrated at the centers thereof. The tank is also provided with an agitator such as the magnetic agitator 10 which maintains the uniformity of the bath.

Into the anode compartments formed by the glass diaphragms is poured a mixture of sulfuric and hydrochloric acids containing no antimony chloride in solution. The density of the solution inside the diaphragms is slightly inferior to that of the electrolytic bath of mixed sulfuric and hydrochloric acids which fills the remainder of the apparatus. In this way, when the equilibrium of pressure is established between the anode and cathode compartments, there is an effective separation of the anode and cathode solutions and the hypochlorous acid formed remains localized in the anode compartments.

The following example illustrates the preferred form of conduct of this process: There were prepared 24 liters of a tartaric solution containing 40 grams per liter of antimony by dissolving 1160 grams of antimony oxide in an aqueous solution containing 160 grams per liter of commercial tartaric acid. This solution was electrolyzed in an electrolytic tank of plastic provided with 5 pure graphite anodes of which the dimensions are 190 x 250 x 10 mm. and 4 cathodes of brass, the dimensions of which were 200 x 250 x 1 mm. For 2 days there was passed through the electrolytic bath a current of 0.6 ampere at -210 millivolts, this potential being measured on a calomel electrode. After this first electrolysis, during the course of which the copper and bismuth were deposited, the bath was flowed into another tank containing 2 platinum electrodes acting as anodes and 3 platinum electrodes acting as cathodes of which the dimensions were 250 x 200 x 0.3 mm.

The second electrolysis proceeded at a potential of -320 millivolts, being constant, the current being 6 amperes at the beginning and 1.2 amperes at the end of the electrolysis. After 6 days there was recovered 810 grams of antimony by removal from the cathode and this was attacked in the cold by means of 2.5 liters of commercial nitric acid, chemically pure. A precipitate of antimony oxide formed and was removed and washed with boiling water, then dissolved in 4 liters of 11 N chemically pure HCl. The product of this acid attack was distilled fractionally until the temperature reached 220°C., this final temperature being maintained for about 5 minutes before arresting the distillation. The antimony chloride recovered from the distillation, free from arsenic, containing about 800 grams of

FIGURE 1: CELL FOR THE MANUFACTURE OF HIGH-PURITY ANTIMONY BY ELECTROLYSIS



Source: R. Beau; U.S. Patent 3,108,934; October 29, 1963

antimony, was dissolved in 3.3 N sulfuric acid and 1.5 N hydrochloric acid so as to prepare 20 liters of a solution containing 40 grams per liter of antimony. This solution was introduced to a plastic tank of the type described above containing 2 platinum cathodes the dimensions of which were 250 x 200 x 1 mm. and 3 pure graphite anodes 27 mm. in diameter and 125 mm. long immersed in $HCl—H_2SO_4$ mixture described above and free from antimony in solution.

The anodes were covered by diaphragms of which the diffuse parts were formed by fritted glass plates of fine porosity. The electrolysis was carried out with intensity varying from 5 amperes to 1.1 amperes at a potential difference maintained at -190 millivolts. After 7 days there were recovered 712 grams of high purity antimony which was melted under a layer of potassium cyanide in a quartz crucible having a ground glass valve. The molten antimony was poured under an atmosphere of argon.

The antimony was of very high purity. Spectrographic analysis revealed only 5 parts per million of iron and 1 part per million of copper. It did not reveal any traces of the other impurities such as arsenic, lead, silver, nickel, zinc, tin, mercury, aluminum and bismuth.

CHEMICAL REDUCTION PROCESSES

It is known that when vapors of antimony pentachloride are passed over molten magnesium, elemental antimony, in the form of shiny globules and crystals, evolves with the emission

of light flashes. It is also known that antimony pentachloride can be reduced to metallic antimony with the aid of finely divided potassium in boiling toluene. Further, when a mixture of $SbCl_5$ vapor and chlorine is burned in hydrogen, a gray-black powder consisting of 93% of antimony and 7% of $SbCl_3$ is obtained. Under conditions of an electrode-less electric discharge, small quantities of antimony metal can also be obtained from $SbCl_5$ and hydrogen.

In the production of relatively large quantities of highly pure antimony as are required for semiconductor materials and devices, antimony chloride, after being subjected to hydrolysis to form antimony pentoxyhydrate, can be converted to the tetroxide by glowing. The latter can subsequently be reduced in a hydrogen current to metallic antimony. However, radiochemical analyses indicate that in the course of the three steps (hydrolysis, glowing and reducing) the amount of metallic impurities is not appreciably diminished.

Siemens-Schuckertwerke AG

A process developed by M. Wilhelm (U.S. Patent 3,168,395; February 2, 1965; assigned to Siemens-Schuckertwerke AG, Germany) involves the production of extremely pure antimony from antimonic chloride which has been carefully purified by repeated vacuum fractionation. A specific object of the process is to greatly increase the yield of antimony per unit time. Another object is to reduce the power requirements for obtaining the desired antimony metal of extreme purity.

According to this process, antimonic chloride, which is vapor heated to a temperature of about 100°C., passes together with dry hydrogen into a reduction zone heated to a temperature of about 700 to about 900°C., and thereafter the metallic antimony is precipitated in crystalline form at a lower temperature, for example, 400° to 500°C. The yield of metallic antimony per unit time is greatly increased by simultaneously adding water vapor to the above mentioned mixture of antimonic chloride vapor and hydrogen.

The added water vapor has the effect of causing the reduction of antimony pentachloride $SbCl_5$ to take place, in the sense of a homogeneous catalysis, with rapidly occurring partial reactions, for example, the formation and reduction of oxychloride or oxyhydrates or oxides. A purified inert gas, for example, argon, laden with water vapor at a temperature of 60° to 80°C. preferably serves as transporting agent for carrying the steam into the reduction zone. The inert gas is charged with steam at a temperature of 60° to 80°C. and is employed, for example, in quantities necessary for the formation of antimony pentoxide. The antimony pentachloride is hydrolyzed in the presence of this water vapor and the thus resulting antimony pentoxide is reduced to antimony while avoiding wet-chemical reactions.

By reaction of gaseous antimonic chloride, which has been repeatedly fractionated, with hydrogen in the presence of quantities of water vapor necessary for the formation of antimony pentoxide, an additional considerable removal in foreign elements is achieved, particularly a reduction in the quantity of magnesium, calcium and silicon impurities. The amount of water required for the method is rather small. For example, for converting 598 g. antimony pentachloride to antimony pentoxide (antimonic oxide) at most an amount of 90 g. water is consumed. The heretofore known wet-chemical purifying method required approximately 6,000 g. of quadruply distilled water for hydrolysis of the same quantity of $SbCl_5$.

This method affords an increase in yield of highly pure antimony of approximately 50% to give a total yield of approximately 70% based on the raw antimony used as starting material. The process, furthermore, eliminates all processing steps which place antimony or antimonic oxide into contact with crucible material such as aluminum oxide. The three-method stages: hydrolysis, partial reduction of antimony pentoxyhydrate and reduction of antimony tetroxide, are performed as a single operation. This achieves a considerable simplification in comparison with the purifying methods heretofore available.

The drawing (Figure 2) shows schematically an apparatus for performing the process. Purified hydrogen is supplied through a pressure limit valve 11 and a flow meter 12 to a trap 13 cooled with liquid nitrogen. The hydrogen, freed from traces of moisture in trap 13 bubbles through the $SbCl_5$ kept in a gas washing flask 14 at 100°C. and then enters into the reaction zone at 15, this zone being kept at about 800°C. The length of the reduction furnace 15 is about 30 cm. In addition to the above, purified argon or purified nitrogen is supplied through a valve 16 and a flow-quantity meter 17 and is charged in a flask 18 with water vapor and is thereafter also passed into the reduction furnace 15.

The bath temperature for the flask 18 is approximately between 60° and 80°C. Only after the addition of moist argon to the mixture of H_2 and $SbCl_5$ vapor, does a rapid reduction to metallic antimony take place. This requires the intermediate formation of antimony-oxygen compounds due to hydrolysis. The precipitation of antimony takes place within the heater furnace 19 whose length is about 13 cm. and whose temperature is kept between 400° and 500°C.

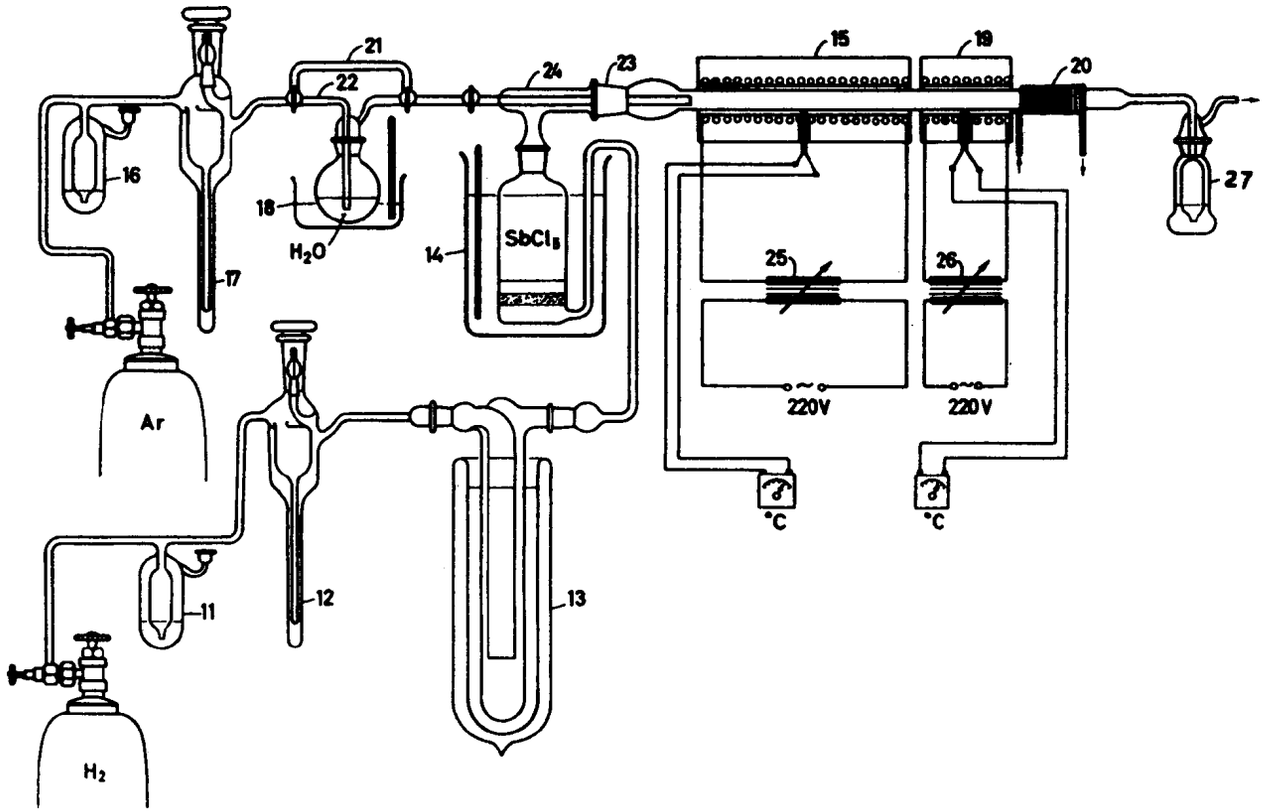
The furnaces 15 and 19 are connected with an alternating-voltage source of 200 v. through control transformers 25 and 26, respectively. The exhaust gases are cooled by coil 20 prior to passing through washing flask 27 and thence from the system.

After introducing 100 ml. pentachloride in gas washing flask 14, the entire apparatus is then rinsed with dry argon or nitrogen, which passes through the connection 21 bypassing flask 18. Thereafter a hydrogen current of 30 to 40 liters per hours is passed through flask 14 and a current of argon or nitrogen, for example, of 4 to 8 liters per hour, is adjusted to flow through the connection 22. The heating paths as well as the reduction furnaces and precipitators are brought to the above-mentioned temperatures.

Particular attention should be given to a good heat insulation of the connecting piece between the water flask 18 and the reduction pipe 23. The temperature of the knee-shaped transfer piece 24 is to be kept at 100°C. by means of a heating jacket or by hot air. Only when these conditions are substantially satisfied is a high yield Sb metal reliably secured.

In a period of one hour the above described method permits entraining about 9 g. $SbCl_5$ which are reduced to antimony metal with an approximate yield of 85 to 90%. Increasing the $SbCl_5$ temperature in the gas washing flask 14 from 100° to 110° to 120°C., as well as a further increase in the H_2 flowing speed, greatly promotes the dissociation of $SbCl_5$ into $SbCl_3$ and Cl_2. It is therefore particularly advantageous, for increasing the Sb yield, to increase the surface of the evaporating pentachloride, for example, by providing a number of gas washing flasks or by employing a number of round bottom vessels in lieu thereof.

FIGURE 2: APPARATUS FOR PRODUCTION OF HIGH PURITY ANTIMONY FROM ANTIMONY CHLORIDE AND HYDROGEN



Source: M. Wilhelm; U.S. Patent 3,168,395; February 2, 1965

ARSENIC

Arsenic is used as an n-type impurity element in the doping of intrinsic semiconductor materials. Arsenic is also an important ingredient of semiconductor compounds. Gallium arsenide in particular, is probably the most promising of the binary-compound semiconductors for all around use. Such intermetallic compounds include indium arsenide and the closely related antimony compounds including indium antimonide, gallium antimonide, etc. Such intermetallic compounds if used for solar batteries, transmitters and rectifiers, infrared detectors, photomagnetic devices, etc. must be of very high purity if they are to function effectively at higher temperatures. Lack of success in using these compounds in many cases is attributed to the difficulties encountered in removing sulfur, selenium and tellurium as impurities from the arsenic or the antimony before reacting it with indium and gallium.

Methods of purifying indium and gallium are well known and no particular difficulties are encountered in producing indium and gallium of high purity. Arsenic and antimony, however, which are usually purified by sublimation of the elements cannot be obtained in sufficiently pure form. The efficacy of the known methods of removing impurities such as the elements of the sulfur group (sulfur, selenium and tellurium) from arsenic and antimony is rather low because the volatile sulfur compounds (As_2S_2 and As_2S_3) and those of antimony (Sb_2S_2 and Sb_2S_3) have about the same volatility as arsenic and antimony respectively; the same is generally true for the corresponding compounds of selenium and tellurium.

ARSENIC TRIOXIDE PURIFICATION

U. S. Army

A process developed by G.A. Wolff (U.S. Patent 2,944,885; July 12, 1960; assigned to the Secretary of the Army) involves purifying arsenic (or antimony) by heating the impure oxides of these metals in the closed end of a tube made of Pyrex glass or quartz to at least the sublimation temperature of the respective oxide whereupon the metal oxide vapor is allowed to fractionally condense along a prolonged path of decreasing temperatures within the evacuated tube to form zones of metal oxide crystals of different degrees of purity. Under these conditions the gaseous metal oxide will deposit within the tube at different distances. There will be a first short zone of rather dark colored crystals of the arsenic or antimony oxide containing all sorts of impurities other than those from the sulfur group. This first zone is followed by a central zone of considerable length of pure crystals of pure white appearance after which comes a third zone of reddish-orange to almost black color