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ELECTROPLATING OF GERMANIUM

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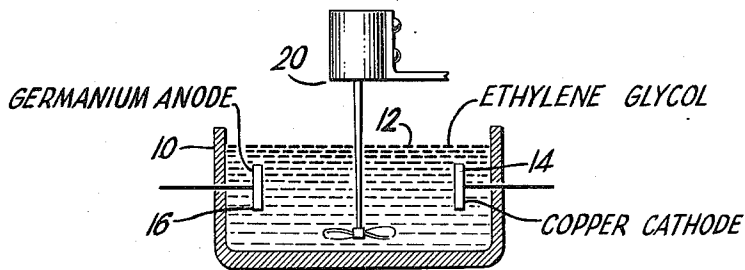


Fig. 1

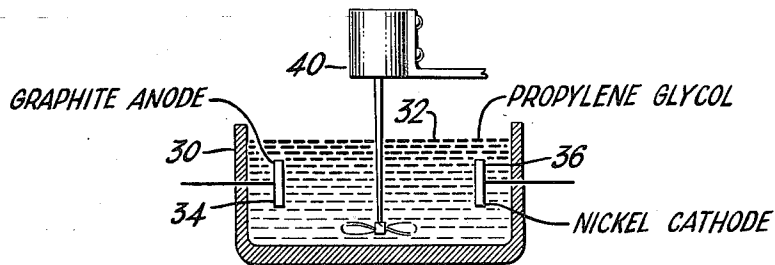


Fig. 2

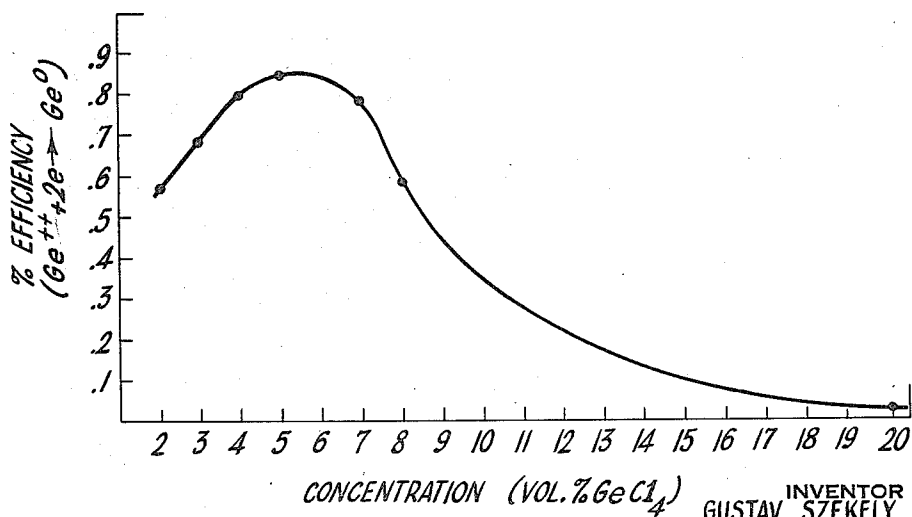


Fig. 3

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ELECTROPLATING OF GERMANIUM

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This invention relates to the electrodeposition of germanium in the form of a bright metallic coating.

Although germanium has been used for some time in the construction of electrical devices such as crystal rectifiers, transistors, photoelectric cells, etc., no satisfactory method of electrolytically depositing germanium had heretofore been devised. Although it is true that germanium had been electrolyzed from ammoniacal ammonium tartrate solutions by the discoverer of the element it was reported to be a poorly adhering germanium film. Subsequently it was found that germanium could be electrodeposited in the form of a coherent steel gray film from aqueous potassium hydroxide solutions of germanium dioxide. After a thin germanium film had been electrodeposited by this method little if any additional germanium could be observed. Further electrolysis apparently yields mostly hydrogen. More recently Fink and Dokras have reported the use of a molten salt bath and several organic baths for the electrodeposition of germanium. The salt bath consists of a molten mixture of borax and germanium dioxide with a graphite rod suspended in the melt to serve as anode and a graphite crucible as cathode. In accordance with this method molten germanium could be collected at the bottom of the crucible. They also report the use of organic baths containing germanium iodide dissolved in glycerine, ethylene glycol or diethylene glycol. Although it is possible to plate germanium from the borax bath which had been described by the authors as a method of electrowinning the element and by doing so to obtain silvery adherent but brittle films of germanium metal, this method is unsatisfactory for the following reasons: Firstly, its operating temperature range includes the melting point of germanium, 958° C. At this temperature metals used as cathodes readily diffuse or dissolve into the bath or into the deposit thus leading to impure germanium. Secondly, as the cathode is withdrawn from the bath a considerable amount of the melt adheres to it making it necessary to go through a lengthy operation of dissolving and leaching.

When the organic germanium iodide bath is used it is necessary to operate the bath at temperatures in the range of 140 to 150° C. At this temperature a considerable decomposition takes place and considerable solvent is lost by evaporation. Furthermore, a large quantity of other compounds deposit with the germanium in the form of a white film of non-metallic appearance which separates out with the steel gray ger-

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manium film. The deposited germanium film flakes off quite easily.

In accordance with this invention it has been found that germanium can be plated out satisfactorily from solutions in the form of a bright metallic coating. This can be accomplished by dissolving germanium tetrachloride in a suitable organic solvent.

An object of this invention is to provide a suitable bath from which germanium can be deposited electrolytically in the form of a bright metallic coating.

A further object of this invention is to provide an improved method of depositing substantial films of germanium electrolytically.

These objects and other advantages can be attained by dissolving germanium tetrachloride in a suitable organic solvent and electroplating the germanium therefrom.

In the drawings which illustrate preferred embodiments of this invention

Figure 1 shows a schematic view of an electroplating bath containing germanium tetrachloride dissolved in ethylene glycol.

Figure 2 is a schematic view of another embodiment of an electroplating bath containing germanium tetrachloride dissolved in propylene glycol.

Figure 3 is a curve showing cathode current efficiency of a propylene glycol bath as a function of concentration.

In the preferred embodiment of the bath illustrated in Figure 1 the tank 10 contains a solution 12 of germanium tetrachloride in ethylene glycol from which germanium is deposited upon a copper cathode 14. The anode 16 used in this bath is of cast germanium. Agitation means is provided therein by means of a motor driven propeller type agitator 20.

In the embodiment illustrated in Figure 2 of the drawings the tank 30 contains a solution 32 of germanium tetrachloride in propylene glycol. The germanium is being plated onto a nickel cathode 36. The anode 34 in this case is made of graphite. A propeller type agitator 40 is there shown for producing the desired agitation in the solution during the plating operation.

When germanium is plated from a solution of germanium tetrachloride prepared in accordance with this invention thick well adhering germanium films can be obtained. These metallic films are of silver mirror-like brightness and are of a high degree of purity. The baths may conveniently be operated at temperatures in the neighborhood of 50–60° C., at which temperature neither decomposition nor appreciable loss of solvent nor solute occurs.

In those cases in which the germanium tetrachloride is dissolved in ethylene glycol the electrodeposition is preferably carried out with the use of a germanium anode of the type as shown schematically in Figure 1 of the drawings. If the best type of coatings are to be obtained more freedom of action is possible in those cases in which propylene glycol is used as the solvent for germanium tetrachloride. In these cases very good coatings of germanium can be obtained with graphite anodes as well as with germanium anodes. There is reason to believe that substances like 1,2 butanediol or 1,2 pentanediol might serve as solvents for germanium tetrachloride in the preparation of a plating bath.

Although germanium tetrachloride is quite soluble in ethylene glycol it has been found desirable to keep the bath concentration relatively low if good plating is to be obtained. If the concentration of the mixture is too high, for example, in the neighborhood of 10 vol. percent germanium tetrachloride a precipitate of white crystals is formed upon standing. However, to achieve good results the concentration should be kept above .5 vol. percent of germanium tetrachloride if the bath is to be operated at a cathode current density of 0.2 amp./cm.² and a temperature of about 50° C. At .5 vol. percent and below the deposits obtained are dull, gray, and rough. When the concentration goes as low as .1 vol. percent black smutty deposits are obtained. The cathode current efficiency and appearance of deposits as a function of concentration in the germanium tetrachloride-ethylene glycol bath can best be shown by the following table:

Initial Concentration (Vol. Percent GeCl ₄)	Average Conc. During 30 Min. Run Based Upon Anode Efficiency Data (g. Ge/100 cc.)	Cathode Current Efficiency (Percent) $\text{Ge}^{++} + 2e \rightarrow \text{Ge}^0$
3.0	2.06	.53
1.5	1.11	.44
1.0	0.79	.23
0.5	0.47	.18

50 ml. volumes solution were electrolyzed at a cathode current density of 0.2 amp./cm.², a temperature of 50° C. and agitation. Ge anode, Cu cathodes.

The influence of current density and temperature on deposition in the germanium tetrachloride-ethylene glycol bath can best be seen from the following table.

Temperature (° C.)	Current Density (amp./cm. ²)	Observations
21-26	0.05	Deposition first observed if cathode is exposed to high agitation.
	0.15	First bright film.
	0.24	Bright deposition.
	0.07	Deposition first observed.
53-56	0.11	Bright deposition.
	0.15	
	0.15	
	0.20	
	0.30	
	0.05	No deposit.
78-80	0.10	Deposition first observed.
	0.20	Bright deposits but of coarser grain than at lower temperatures. (The rate of solution of the stop-off used becomes larger at higher temperatures; this indirect effect of temperature may also have been responsible.)

Plating Conditions: Conc.=3.8 vol. percent GeCl₄ throughout. The bath was agitated.

From the above table it is apparent that bright deposits can readily be obtained at a current density from about 0.1 amp./cm.² upwards. It has been found that an increase in temperature causes a large increase in cathode current efficiency so that a bath operated at about 90° is approximately four times as efficient as one operated at 50°.

If bright silvery deposits are to be obtained it is recommended that the bath be agitated. However, the rate of agitation at the cathode has no significant effect upon cathode current efficiency.

For best results it is important that the moisture content of the bath be controlled for if the water content should reach 20 milligrams of water per cc. no appreciable germanium will be deposited. In working with this bath it has been found that silver-like deposits of germanium can be plated on cathodes of many different types including copper, nickel, aluminum nickel alloy, zirconium, and graphite, etc. Furthermore, the throwing power of the bath seems excellent.

It has been further found that when platinum is made anodic in this bath it dissolves. For these reasons it may prove useful for the codeposition of platinum and germanium. Although graphite may be used as the anode in the ethylene glycol-germanium tetrachloride bath the desired bright coating is not as readily obtained as when propylene glycol is used in place of ethylene glycol. However, when the germanium anode is used and the germanium concentration is adjusted below the point where precipitation of a white, crystalline substance occurs, bright silvery mirror-like deposits can be obtained continuously from this bath.

While it is obvious that electrodeposition of germanium from germanium tetrachloride-ethylene glycol baths represents a considerable improvement over prior art methods in that the bath deposits uniformly bright metallic germanium which adheres well to the base metal and which does not contain organic or inorganic impurities, and while the bath can be operated at a temperature at which neither the chloride nor the solvent volatilizes to any appreciable extent, the bath does, however, offer several objectionable features in that the use of the germanium anode makes it impossible to plate at constant bath concentration and the high anode current efficiency eventually leads to a precipitation which calls for diluting the bath to permit further operation. These difficulties are overcome by substitution of propylene glycol for ethylene glycol. When this is done no solid phase precipitates either when preparing solutions of high germanium content or upon electrolysis of the bath for long periods of time. This permits the use of higher concentrations in the bath with an actual increase in cathode current efficiency and, hence, of plating speeds.

Furthermore, the rate of water absorption from the atmosphere is smaller for propylene glycol than for ethylene glycol thus making it easier to maintain the efficiency of the propylene glycol bath.

In addition, it has been found that this bath may be operated with graphite anodes without decreasing the brightness of deposits. This permits operation of the bath at essential constant germanium concentration.

It has been found that there is a definite trend toward an increase of brightness of the deposits

with increasing concentration of the germanium tetrachloride; the brightest deposits are obtained with solutions containing 7 vol. percent of germanium tetrachloride in propylene glycol at current densities of 0.2 amp./cm.²–0.4 amp./cm.²

The effect of temperature, current density and concentration upon appearance of deposits and cathode current efficiency of the germanium tetrachloride-propylene glycol bath can best be seen from the following table:

[Effect of temperature, current density and concentration upon appearance of deposits and cathode current efficiency ($\text{Ge}^{++} + 2e \rightarrow \text{Ge}^0$). Germanium tetrachloride-propylene glycol bath.]

Average Temp.	Vol. Percent GeCl_4	0.2 amp./cm. ²		0.3 amp./cm. ²		0.4 amp./cm. ²	
		Appearance of Deposit	Cath. Current Eff. (Percent)	Appearance of Deposit	Cath. Current Eff. (Percent)	Appearance of Deposit	Cath. Current Eff. (Percent)
50.2° C.	3	a. metallic silvery.....	0.558	bright with white hue....	0.571	considerable amt. of streaking over bright surface.	0.524
	5	metallic silvery (brighter than a).	0.621	bright with slight streaking over entire surface.	0.685	mirrorlike minute streaking over surface, some streaking near.	0.773
	7	b. metallic silvery (brighter than a).	0.654	very bright.....	0.689	mirrorlike.....	0.818
59.3° C.	3	bright whitish hue in part.	0.750	bright with good amt. of streaking over surface.	0.660	large amt. of streaking over entire surface.	0.651
	5	brighter than b, but not mirrorlike.	0.868	almost mirrorlike with slight streaking near edges.	0.773	almost mirrorlike with slight streaking near edges.	0.877
	7	very bright but not mirrorlike.	0.713	mirrorlike.....	0.810	perfect mirror.....	0.843

Moisture content of propylene glycol=0.2 mg. $\text{H}_2\text{O}/\text{ml}$.
Cathode surface speed=10 m./min.
Graphite anode.

The cathode current efficiency of the propylene glycol bath at 60° and at a current density range of 0.2–0.4 ampere per square centimeter is best seen in Figure 3 of the drawings.

It has been found that if the water concentration of the bath is increased from .3 gram per liter to 1.3 grams per liter it will cause a reduction in cathode current efficiency of approximately 8.7%. The cathode current efficiency of a propylene glycol bath is clearly shown in Figure 3 of the drawings. As there shown the maximum efficiency is obtained within the relatively narrow range of 2 to 8 volume percent of the germanium tetrachloride. At concentrations above this range the efficiency of the bath falls off very markedly. The peak efficiency lies at about 5% with an optimum range of about 4 to 7%.

At optimum conditions for bright plating from the propylene glycol bath, 7 vol. percent, 59° C., 0.4 amp./cm.² using agitation and a graphite anode, germanium deposits at the rate of 0.001" per three hours. It is noteworthy that germanium can be deposited from propylene glycol baths to a thickness of 0.005" and still show the bright plated appearance. From the above it can be seen that while the propylene glycol baths give deposits similar to those from ethylene glycol baths they show none of the difficulties of operation inherent in the ethylene glycol bath.

It is of course to be expected that various changes, alterations and modifications will occur to those skilled in the art upon reading the present disclosure. It is to be understood, however, that the modifications disclosed herein are described for illustrative purposes only and are not intended to limit the scope of the appended claims.

What is claimed is:

1. A bath suitable for the electrodeposition of germanium at temperatures below 90° C. comprising a .5 to 10 volume percent solution of ger-

manium tetrachloride in an alkyl glycol whose hydroxyl groups are present in the 1,2 position.

2. A bath suitable for the electrodeposition of germanium at temperatures below 90° C. comprising a .5 to 10 volume percent solution of germanium tetrachloride in ethylene glycol.

3. A bath suitable for the electrodeposition of germanium at temperatures below 90° C. comprising a .5 to 10 volume percent solution of germanium tetrachloride in propylene glycol.

4. A bath suitable for the electrodeposition of germanium at temperatures below 90° C. comprising a .5 to 10 volume percent solution of germanium tetrachloride in 1,2 butanediol.

5. A bath suitable for the electrodeposition of germanium at temperatures below 90° C. comprising a .5 to 10 vol. percent solution of germanium tetrachloride in ethylene glycol.

6. The method of electroplating germanium from a .5 to 10 volume percent solution of germanium tetrachloride in ethylene glycol held at a temperature below 90° C. comprising passing a current from a germanium anode to the metal base to be plated.

7. A method for producing a bright germanium plating on a metal base which comprises passing a current of .2 to .4 amp./cm.² from a germanium anode to the metal base to be plated through a bath formed essentially from a .5 to 7 vol. percent of germanium tetrachloride in ethylene glycol while said bath is held at a temperature below 90° C.

8. A method for plating germanium from a .5 to 10 volume percent solution of germanium tetrachloride in propylene glycol which comprises passing a current from a graphite anode to the metal base to be plated while said solution is held at a temperature below 90° C.

9. A method for producing a bright germanium plate on a base metal which comprises passing a current of 0.4 amp./cm.² from a graphite anode to the metal base to be plated through a bath formed essentially of a 7 vol. percent solution of germanium tetrachloride in propylene glycol while said solution is held at a temperature below 90° C.

10. A method for plating germanium from a .5 to 10 volume percent solution of germanium tetrachloride in 1,2 butanediol which comprises passing a current from a graphite anode to the metal base to be plated while said solution is held at a temperature below 90° C.

11. A bath suitable for the deposition of germanium at temperatures below 90° C. comprising 3-8 vol. percent of germanium tetrachloride in propylene glycol.

12. A method of electroplating germanium from a .5 to 10 volume percent solution of germanium tetrachloride in propylene glycol comprising passing a current from a germanium anode to the metal base to be plated while said solution is held at a temperature below 90° C.

13. A method for producing a bright germanium plating on a metal base which comprises passing a current of .2 to .4 amp./cm.² from a germanium anode to the metal base to be plated through a bath formed essentially of 3 to 8 vol.

percent of germanium tetrachloride in propylene glycol while maintaining said bath at a temperature below 90° C.

14. A method for producing bright germanium plating on a base metal which comprises passing a current of 0.4 amp./cm.² from a germanium anode to the metal base to be plated through a bath formed essentially of a 7 vol. percent solution of germanium tetrachloride in propylene glycol, said bath being operated at a temperature below 90° C.

References Cited in the file of this patent

Trans. of the Electrochemical Society, vol. 95, 1949, pages 80 and 88-92 inclusive.