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The Technique for Preparing High-Quality Contacts on Lead Tin Telluride

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The conditions and modes of preparing high-quality electric contacts on lead tin telluride wire crystals by chemical deposition of metals (in particular, nickel) are described. By an experimental approach, we found a technique for the preliminary preparation of sample surface, which includes etching, degreasing, activation, and deposition of a nickel underlayer. The conditions of heat treatment of samples for improving the adhesion strength and decreasing the contact resistance are given.

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Introduction

Semiconductor solid solutions of lead telluride and lead tin telluride have been and still are promising materials as regards their use in photoelectric, thermoelectric, and laser technology. Therefore, PbTe and PbSnTe, as well as multicomponent systems based on them, particularly films and wire crystals, have been intensively studied in recent years [1-4]. Various types of sensors and photodetectors have been designed on the basis of single crystals and epitaxial layers of PbTe and PbSnTe. However, the problem of preparing sensors based on lead tin telluride with reproducible and reliable parameters cannot be considered solved. The advance in modern microelectronics is determined by the successful solution of the problem of forming high-quality metal-semiconductor contacts.

There are many techniques and methods for preparing electric contacts: fusing, electrochemical and chemical deposition, vacuum evaporation, ultrasound, overlay laser welding, etc.; each of them has its range of application, advantages, and disadvantages [5-7].

PbTe and PbSnTe and some other semiconductors have a hard-to-remove and easily reducible oxide film on the surface and a deeply negative electrode potential; therefore, electric contacts on them are made in vacuum, in inert or hydrogen atmosphere; however, in this case, energy consumption increases significantly and the process becomes more involved. The method of chemical deposition of metals enjoys wide application in engineering for preparing metal-semiconductor electric contacts; it is relatively simple and reproducible and does not require sophisticated expensive equipment [8].

The aim of this work is to develop a technique for preparing high-quality electrical contacts on lead tin telluride, chiefly on wire crystals on its basis, by chemical deposition of metals (in particular, nickel).

Chemical plating with nickel, as compared to other metals and alloys (Ag, Cu, Au, In, Pd-Ag, Ag-Au, etc.), provides a durable, uniform, nonporous layer with a desired thickness and high resistance to corrosion. In addition, electrodeless nickel plating allows obtaining smooth layers on samples of any geometrical shape; other metals and alloys may be deposited on these layers immediately, thereby simplifying the subsequent processes [5, 6].

I. Experimental Results and Discussion

In this work, we describe the technique of chemical deposition of nickel for preparing electric contacts on PbSnTe and wire crystals (WCs) grown by filling dead-end evacuated quartz capillaries with liquid melt of PbSnTe under pressure of an inert gas with subsequent directional crystallization. The diameters of WCs under study ranged within 10-60 μm; they were single crystals with the [100] preferential direction of growth [4].

It is known that, using standard techniques of surface preparation, it is impossible to obtain tightly adherent chemically deposited layers on PbTe and other alloys containing more than 1-2% lead or cadmium even by contacting with other metals being more electronegative than nickel or activated in a solution of palladium chloride.

Based on experimental studies, we have found conditions and modes of preparing high-qualitative contacts; they consist of two stages:

(a) the sample surface pretreatment that includes etching, degreasing, activation, and deposition of an underlayer of nickel;

(b) chemical deposition of nickel.

The chemical deposition of nickel was carried out both on wafers of bulk PbSnTe single crystals and on the face planes of WCs. For this purpose, samples of WCs in a glass insulation were glued vertically in matrices by 50-100 wires. Note that, in the process of work, we have developed a special technique for mechanical treatment of the end surfaces of WCs. It is based on chemical-mechanical polishing of WCs in a solution based on glycerol, ammonium chloride, and potassium dichromate not involving the process of mechanical polishing; this technique reduces the damaged layer depth to a minimal value of 2 μm, whereas after mechanical polishing this value is up to 20 μm.

Before proceeding to the deposition of an underlayer of nickel, after the chemical-mechanical polishing, we subjected the sample surface to degreasing in an alkali solution of the following composition: 10 g/l $Na_2CO_3 \cdot 10H_2O$ and 20 g/l $Na_3PO_4 \cdot 12H_2O$, at T = 30-40°C during 2-3 min.

After that, the samples were washed thoroughly with deionized water, immersed in boiling isopropyl alcohol, and treated in alcoholic fumes.

The samples were etched in a solution of 10 parts of (95% HBr + 5% Br) and one part of toluene. Toluene contributes to the intensity of dissolution and eliminates formation of oxide film on the sample surface [9]. The polishing process was completed by thorough washing of enchant with acetone and then with deionized water. After that, the samples were immersed into a 10% HBr solution at a temperature of 18-20°C during 10-30 s. With a view to avoiding the formation of an oxide film, the samples were immediately subjected to contact nickel plating in a solution containing hydrobromic acid and nickel chloride.

Upon immersion of the samples in this solution, there take place dissolution of oxides from the surface and precipitation of an underlayer of nickel with grayish-blue tint on the clean surface. It is pertinent to note that the nickel underlayer not only significantly decreases the value of contact resistance at the average values of resistance of lead tin telluride but also leads to approximately the same contact resistance. Presumably, this indicates that a potential barrier in the formation of a contact is the (Br-Ni-Cl)/PbSnTe interface [10].

On the nickel underlayer on the sample surface treated by the technique specified, we deposited nickel from the phosphate solution of the following composition (g/l): 24 $NiCl \cdot 6H_2O$, 35 $NaH_2PO_2 \cdot H_2O$, 25 NH_4Cl, and 30 5% solution NH_4; pH = 8.9; the solution temperature was 25-30°C.

As a result of microscopic studies, the optimum conditions for obtaining uniform and nonporous high-quality surfaces were found. To improve the quality of deposition and to hasten the process of nickel plating, it is necessary to stir the solution continuously with a magnetic stirrer. The nickel layer thickness may be varied within 0.05-100 μm. The layer thickness depends on the rate of rotation of the magnetic stirrer. The temperature of the working solution must be constant (25-30°C) throughout the entire process of deposition, because an increase in the solution temperature leads to deterioration in the adhesion strength; a low temperature results in a brittle coating. The solution pH must be kept constant within 8.9-9, because at pH = 5-6 the coating is loose; at pH > 9 the coating is dark-colored and poorly adheres to the material.

To improve the adhesion strength and to decrease the contact resistance, the heat treatment in vacuum of $5 \cdot 10^{-6}$-$1 \cdot 10^{-5}$ mm Hg was carried out at 120-200°C for 20-30 min. To avoid high mechanical stresses, the cooling rate did not exceed 10 deg/min. The resultant layer is mechanically strong and uniform; it is suited for connecting electrical leads. After the heat treatment, it is possible to deposit other metals or alloys (gold, platinum, copper, silver, etc.) by chemical or other methods that allow connecting electric contacts to WCs.

The adhesion strength of the nickel layer, which is determined by tearing the copper microwires with a diameter of 50 μm soldered to microcontacts, was 6-8 kg/mm^2. Micrographic investigation of the microcontacts showed that it is appropriate to deposit nickel with a thickness of 8-20 μm, because in the case of thickness of 3-5 μm, the nickel layer in the course of soldering was dissolved by the solder in some places.

The use of the described technique of surface preparation makes it possible to obtain high-quality contacts both on bulk samples of lead tin telluride and on films and WCs in a glass insulation obtained of these alloys.

This technique is of particular practical importance for preparing microcontacts on thin wires, because it is simple, low-cost, and environmentally friendly; it allows automating the process of obtaining of high-quality and durable microcontacts of desired sizes on a large number of wires simultaneously.

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Технологія виготовлення якісних контактів на телуриді свинцю та олова

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Наведено умови ї режими виготовлення якісних електричних контактів на ниткоподібних кристалах телуриду свинцю-олова хімічним осадженням металів (зокрема, нікелю). Експериментальним шляхом було знайдена методика попередньої підготовки поверхні зразків, що включає травлення, знежирення, активацію і осадження підшару нікелю. Наведено умови термообробки зразків для підвищення міцності зчеплення та зменшення опору контактів.