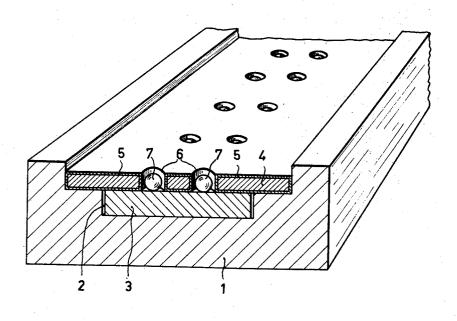
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#### D. DE NOBEL ALLOYING-JIG FOR ALLOYING CONTACTS TO SEMI-CONDUCTOR BODIES Filed July 19, 1960

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1

### 3,080,841 ALLOYING-JIG FOR ALLOYING CONTACTS TO **SEMI-CONDUCTOR BODIES**

Dirk de Nobel, Eindhoven, Netherlands, assignor to North American Philips Company, Inc., New York, N.Y., a Claims priority, application Netherlands Aug. 25, 1959 3 Claims. (Cl. 113-99)

The invention relates to an alloying-jig for alloying contacts to semi-conductor bodies, in particular for the manufacture of transistors, crystal diodes, and similar semi-conductor electrode systems, and in addition to a method of manufacturing such a jig. An alloying-jig is 15 to be understood to mean here apparatus or a device in which one or more spaces are recessed which may serve for receiving semi-conductor bodies and in which in addition one or more apertures are available for fixing the material for the contacts. Beforehand, this material has 20 mostly been shaped as pellets or wafers which may have a diameter of for example a few tenths of a millimeter. Alloying itself is carried out by transferring the jig into an oven and then subjecting it to the required heat treatment. 25

The alloying-jigs are usually manufactured from graphite, because this material can be prepared with a very high degree of purity and such a purity is an important factor in the relative branch of the technology. In addition, graphite is not wetted by the melted contact mate- 30 rial. However, in comparison with the very small apertures which have to be made in the jig, graphite is of coarse grain. Owing to the small strength of the graphite, the jig is highly subject to wear. In addition, graphite may easily absorb contaminating gases and vapours, so 35 that the jig has to be annealed repeatedly when using it frequently.

It has already been suggested to manufacture alloyingjigs of stainless steel, in particular of chrome iron steel, 40 which is coated with a corrosion resistant oxide film. Such jigs can be manufactured with a high degree of accuracy and are subject to only little wear. The oxide film prevents the steel from being wetted by the melted contact material. It has appeared, however, that this 45 oxide film may be partially reduced in the hydrogen atmosphere used during alloying, so that such a jig can be subjected only for a short time to a treatment at alloying temperatures, which, moreover may not be too high, the oxide film having to be regenerated practically after each 50 alloying treatment. In addition, the coefficient of linear expansion of most kinds of stainless steel are larger than  $10 \times 10^{-6}$ , which is much larger than the coefficients of expansion of the commonly used semi-conductor materials, such as germanium and silicon which amount to  $6.1 \times 10^{-6}$  and  $4.2 \times 10^{-6}$  respectively. So the danger 55 exists that during the cooling from the alloying temperature to room temperature the contacts applied may be pushed off by uneven shrinkage of the jig and the semiconductor body.

One of the objects of the invention is to supply a material for jigs for alloying which does not have the above draw-backs, is easy and accurate to machine, and has a coefficient of expansion differing only slightly from that of the commonly used semi-conductor materials, such as 65 germanium and silicon.

The invention is based on the recognition that molybdenum would be extremely suitable for the above purposes. Its coefficient of linear expansion amounts to approximately  $5 \times 10^{-6}$  and consequently differs slightly 70 from that of germanium or silicon. In addition, molybdenum is highly refractory and not readily deformable.

2

Although molybdenum is rather hard, it is readily machinable with normal hard steel tools. However, molybdenum is wetted by melted contact material. The invention is based on the further recognition that molybdenum can very well be coated with a refractory, non-metallic film which is not wetted by molten contact material.

Such a film on molybdenum turned out to be readily resistant to varying temperature treatment to which jigs for alloying are usually exposed. The application of such a film on molybdenum has already been proposed for 10 corrosion resistant purposes. The invention is based on the further recognition that on molybdenum a skin can be provided which, in contrast with the corrosion resistant oxide film of stainless steel jigs, is substantially not reduced by hydrogen.

The alloying-jig according to the invention consists at least partially of molybdenum the surface of which is at least partially provided with a film of refractory, nonmetallic material which substantially cannot be reduced by hydrogen.

According to a preferred embodiment, the film has been obtained by applying a material with which the molybdenum of the base forms a genetic layer. A genetic layer is to be understood to mean herein a layer mainly consisting of a reaction product between one or more compounds of the material of the base to which the layer is applied and a material which has been contacted to the surface of that base. In this case the adhesion of the film on the molybdenum base is particularly strong and the genetic layer may form the whole film or a part of it adjoining the metal.

Preferably, the material to be applied for the formation of the film is deposited from the gaseous phase, as a result of which very slight film thicknesses can be obtained, so that in the mechanical processing of the molybdenum for shaping the jig the thickness of the film to be applied need not be taken into account. A suitable film may be formed for example by depositing carbon. The film is preferably formed by depositing silicon or silicon and carbon. Such films have turned out to be very lasting.

It has appeared that such an alloying jig is very useful inter alia at temperatures above 700° C. for example up to 900° C. and higher, for example 1100° C. in a hydrogenous atmosphere. As a result, the jig is particularly suitable for use in alloying contacts to silicon bodies. However, its use is not restricted to this particular semiconductor material. It is also readily usable in alloying contacts to germanium bodies and in particular renders a very accurate location of the contacts and temperatures of at least 700° C. are possible, also during the long periods required for forming diffusion layers underneath the alloying contacts. For such high temperatures and long heating times, the known stainless steel jig is not suitable.

Since the coefficient of linear expansion of molybdenum differs little from that of semi-conductor materials, such as germanium or silicon, the jig may be used in particular for alloying several contacts distributed over a relatively large surface of for example a plate-like and/or strip-like semi-conductor body without one or more of the contacts applied being pushed off on cooling after alloying owing to shrinkage of the jig even if the largest distances between apertures for fixing the contact material should amount to 1 cm. or more.

In order that the invention may be readily carried into effect, it will now be described in greater detail by way of example with reference to the accompanying drawing.

The FIGURE shows an alloying-jig on an exaggerated scale, partly in vertical section, partly in perspective.

In the figure, 1 is a graphite plate with a recess 2 in which a strip-like semi-conductor body 3, for example,

of n-type or p-type silicon, is laid. On the plate 1 is a molybdenum plate 4 provided with a non-metallic surface film 5 of one of the above described kinds, which plate is provided with apertures 6.

The inner walls of the apertures 6 are likewise coated 5 with the surface film 5. The apertures 6 contain pellets 7 of contact material. For example, they may be of aluminum, or lead antimony, or any of the well-known contact materials for silicon. The assembly may be transferred to an oven in a normal manner, in which, 10 for example at a temperature of 900° C. in a hydrogen atmosphere, the pellets 7 melt within the apertures 6 and alloy to the silicon body 3.

The alloying time may vary between 1 and 30 minutes. It has appeared to be well possible to make apertures 15 having a diameter of  $100\mu$  and a mutual spacing of  $50\mu$ also in a molybdenum plate of for example  $100-200\mu$ thick. Such dimensions can practically not be achieved when using graphite.

The surface film 5 may be applied in a known manner. 20 For example, the molybdenum plate 4 provided with apertures was heated at 1000° C. and a gas current, composed of 10 parts by volume of hydrogen and one part by volume of a gas mixture consisting of hydrogen which was saturated at room temperature with vapour of silicon tetrachloride, was passed along the plate for 10 minutes, after which the resulting layer was reannealed at a temperature of between 1250° C. and 1300° C. for about 10 minutes in pure hydrogen.

Another film of good quality was obtained by first <sup>30</sup> treating the molybdenum part in the above manner at 1000° C. with SiCl<sub>4</sub>-vapour and hydrogen and then treating with a gas mixture consisting of 10 parts by volume of hydrogen and 1 part by volume of butane for 5 minutes at the same temperature after which the layer was reannealed in the above-manner. With the resulting film, the jig turned out to be well useful at a temperature of 1100° C.

Both processes are believed to produce a molybdenum silicide or disilicide coating or plating on the molybdenum. The technique described is sometime referred to as vapour-plating. Other suitable coatings include  $B_4C$ , SiC, MoC, Mo<sub>2</sub>C, which similarly may be formed by a vapour-plating process, which involves reducing or decomposing a volatile compound of the coating material upon the heated molybdenum body or specimen, depositing an adherent coating of the non-volatile reaction products.

What is claimed is:

50 1. Apparatus for fusing contact material to impuritysensitive semiconductive bodies in a hydrogen-containing atmosphere, comprising support means for receiving and supporting a semiconductive wafer, and a member arranged generally parallel to and mounted on said support and having a surface-coated molybdenum portion overlying and contacting a surface of said wafer, said

member containing an aperture overlying the wafer surface for receiving and positioning a mass of contact material in engagement with the wafer surface for melting within said aperture, said surface-coating on the molybdenum

portion being an adherent non-metallic refractory surface film selected from the group consisting of molybdenum carbides, molybdenum silicides, silicon carbides, and boron carbide, and which is not wetted by the molten contact material and not substantially reduced by hydrogen.

2. Apparatus for fusing contact material to impuritysensitive semiconductive bodies in a hydrogen-containing atmosphere, comprising support means for receiving and supporting a semiconductive wafer, and a thin plate arranged generally parallel to and mounted on said support and having a surface-coated molybdenum portion overlying and contacting a surface of said wafer, said plate containing an aperture overlying the wafer surface for receiving and positioning a mass of contact material in engagement with the wafer surface for melting with-

in said aperture, said surface-coating on the molybdenum portion being an in-situ formed adherent non-metallic refractory surface film selected from the group consisting of molybdenum carbides, molybdenum silicides, silicon carbides, and boron carbide, and which is not wetted by the molten contact material and not substantially reduced by hydrogen.

3. Apparatus for fusing contact material to impuritysensitive semiconductive bodies in a hydrogen-containing atmosphere, comprising support means for receiving and supporting a semiconductive wafer, and a molybdenum plate arranged parallel to and mounted on said support and having a surface-coating and overlying and contacting a surface of said wafer, said plate containing a pair of apertures spaced apart and overlying the wafer surface for receiving and positioning a pair of masses of contact material in engagement with the wafer surface for melting within said apertures, said surface-coating on the molybdenum plate being an in-situ formed adherent nonmetallic refractory surface film selected from the group consisting of molybdenum carbides, molybdenum silicides, silicon carbides, and boron carbide, and which is not wetted by the molten contact material and not substantially reduced by hydrogen.

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4