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(54) **PASSIVATING ETCHANTS FOR METALLIC PARTICLES**

PASSIVIERUNGSÄTZMITTEL FÜR METALLPARTIKEL

AGENT D'ATTAQUE CHIMIQUE ASSURANT LA PASSIVATION DESTINE A DES PARTICULES  
METALLIQUES

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**WO-A-92/08561 US-A- 4 410 569**  
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**US-A- 5 387 315 US-A- 5 980 983**

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- **GEORGE M A ET AL: "REACTION OF 1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONE (H+HFAC) WITH CUO, CU2O, AND CU FILMS" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 142, no. 3, 1 March 1995 (1995-03-01), pages 961-965, XP000504904 ISSN: 0013-4651**
- **DATABASE CA[Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LEDBETTER, JAMES WILLIE, JR.: "The effects of temperature and reactive environments on metal particle sintering and redispersion" retrieved from STN Database accession no. 131:7039 XP002183190 & (1998) 350 PP. AVAIL.: UMI, ORDER NO. DA9904519 FROM: DISS. ABSTR. INT., B 1999, 59(9), 4962,**

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**EP 1 066 416 B9**

## Description

### Technical Field.

**[0001]** This invention relates to thin film silicon solar cells and methods for forming particle-derived ohmic contacts with p-type silicon. A process is provided for etching the oxide or hydroxide corrosion layer from the surface of metallic particles, such as aluminum, which is shown to improve the electrical properties of the contacts to the p-type silicon.

### Background Art.

**[0002]** While various methods for the production of particle derived thin-films have been reported, the thin-film application of these materials in microelectronics has been hampered by a lack of good interparticle connectivity when applied as films to substrates. This connectivity, both structural and electrical, is in many cases limited by the formation of a corrosion layer (i.e., oxide or hydroxide) contaminating the surface of the particles. These passivated surfaces generally give rise to an insulating effect electrically and an impedance in particle sintering structurally.

**[0003]** In order to form a thin-film for use in photoconversion and microelectronic device applications, the regions coated with particles are typically sintered to ensure electrical continuity across the feature. A reduced melting temperature for nanophase metals (C.R.M. Wronski, *Brit. J. Appl. Phys.*, (1967)18:1731; J. F. Pocza, A. Barna and P. B. Barna, *J. Phys. F.* (1972)2:441) and semiconductors (A. N. Goldstein, C.M. Echer and A. P. Alivisatos, *Science*, (1992)256:1425; and A. N. Goldstein, Ph. D. dissertation, University of California at Berkley (1993)) has previously been shown. These disclosures are incorporated by reference herein. High temperature sintering often eliminates some of the problems associated with surface contamination. However, in the formation of nanoparticle contacts with photovoltaic semiconductors, standard high-temperature sintering often cannot be performed due to thermal limitations which are associated with the underlying layers of the device.

**[0004]** In view of the foregoing considerations, there is an apparent need for a low temperature method for etching the corrosion oxide or hydroxide layers. Etching improves the electrical conductivity across the feature and is useful in the formation of particle-derived ohmic contacts, such as aluminum, with a p-type silicon layer of silicon solar cells. The formation of a post-etch passivation layer impedes further corrosion and renders the particles stable to oxidizing and hydrous environments. Accordingly, a primary object of the present invention is to provide a method for etching a metallic particle surface to remove the corrosion layer to form a post-etch passivating layer on the particles, and, ultimately, to improve electrical conductivity of metal contacts.

**[0005]** Another object of the present invention is to pro-

vide an improved method for forming ohmic contacts derived from metallic particles, such as aluminum, with a p-type silicon layer of a silicon solar cell.

**[0006]** These and other objects of the present invention will become apparent throughout the description of the invention which now follows.

### Disclosure of Invention.

**[0007]** The present invention provides a process for etching a corrosion layer, such as oxide or hydroxide, from and concomitantly forming a passivating layer on the surface of metallic nanoparticles. A reaction mixture is prepared by dispersing, sodium hexafluoroacetylacetonate (Na(hfa)) and a metallic particle powder having oxide or hydroxide corrosion layers in hexane solvent. The mixture is allowed to react for a time sufficient to etch the oxide or hydroxide groups from the particulate surface and passivate the surfaces with (hfa). Hexane may be evaporated from the mixture and any excess Na(hfa) separated from the reaction mixture by sublimation or rinsing with a polar aprotic solvent. In an embodiment of the present invention, aluminum particles are first etched and passivated and then used to form ohmic contacts with p-type silicon. This etching/passivation improves the electrical properties of the contact.

### Brief Description of Drawings.

#### **[0008]**

Figure 1 shows the current-voltage characteristics of a solar cell where particulate aluminum is slurried onto p-type Si and annealed at 645° in argon for one hour. This is the control sample.

Figure 2 shows the current-voltage characteristics of a solar cell where particulate aluminum is etched/passivated with Na(hfa), according the method of the present invention, slurried onto p-type Si, and annealed at 649° in argon for one hour.

### Description of the Preferred Embodiments.

**[0009]** While it is within the scope of the present invention to use particles of a greater size, in the preferred embodiment nanoparticles are used. A nanoparticle is a particle having dimensions in the nanometer range, that is, of less than 10nm. While materials in this size range may be utilized, the preferred size range is from 3-8 nm. The nanoparticles include, without limitation, all metals and alloys having useful properties as contacts to semiconductors, such as Ni, Au, Al, Ag, and Au-Ga. The particle derived ohmic contacts, according to the invention herein, can be formed on any suitable surface or substrate, for example on carbon, silicon, germanium, III-V semiconductors, II-VI semiconductors, and I-III-VI<sub>2</sub> semiconductors. These compounds, and their application in solid state electronic devices, are well known. All refer-

ences herein to a Class of compounds herein refers to the Class of Elements as set forth in the Periodic Table of the Elements, published by the American Chemical Society. The disclosure of all patents cited herein are incorporated by reference.

**[0010]** The present invention provides for etching a corrosion layer, such as oxide or hydroxide, from and concomitantly forming a passivating layer on the surface of metallic particles. Ohmic contacts formed by slurry deposition of a Na(hfa) etched/passivated particulate aluminum powder, and annealed with p-type Si provides one example of an ohmic contact having desirable current-voltage characteristics. The example which follows describes in detail the process for preparing Na(hfa)-etched/passivated aluminum particles.

#### EXAMPLE

**[0011]** A particle aluminum reaction mixture was prepared by dispersing 0.12 g Al particulate powder into a mixture comprising 11.0 g hexafluoroacetylacetonate in approximately 150 ml hexane. An aliquot of NaH was added to the reaction mixture and the mixture was allowed to react approximately twelve hours with stirring under nitrogen gas aeration. These mixing conditions provided a sufficient time for etching of the oxide and/or hydroxide groups from the Al particles an concomitant formation of a passivation layer. Hexane supernatant was then decanted from the reaction mixture and the remaining suspension was separated by centrifugation at 2,600 rpm for 10 minutes. Supernatant fluid was then decanted from the centrifuge tube and the remaining solvent removed in vacuo. The remaining solid was transferred to a Dailey Sublimier in a He-filled globe box. The sublimier was placed onto a Schlenk line and evacuated to  $10^{-3}$  torr. An oil bath was employed and the mixture was heated to 200°C. At this temperature, the unreacted Na(hfa) sublimed up to the cold finger leaving Na(hfa)-treated Al particles in the bottom. FTIR spectroscopy of a sample of Na(hfa)-treated Al showed peaks due to the hfa ligand. TEM-EDS showed a marked reduction in oxygen content as well as the appearance of fluorine.

**[0012]** Na(hfa)-treated Al powder was then applied to p-type Si to check for ohmic contact. A control sample was prepared using untreated Al powder on p-type Si. In both instances, an aliquot of Al was slurried with hexane in a He-filled glovebox and dropped onto the Si wafer. These samples were transferred to a tube furnace, the tube was purged with argon, and the samples were heated for one hour at 645-649°C. After the contact anneal, the residue that remained where the Al slurry was dropped, was removed using an isopropanol-wetted Q-tip. Silver paint was added to these regions and I-V characterization was performed.

#### Claims

1. A process for etching the corrosion layer form and concomitantly forming a passivating layer on the surface of metallic particles comprising:
  - a) forming a reaction mixture by dispersing sodium hexafluoroacetylacetonate and metallic particles having oxide or hydroxide corrosion layers, in a solution comprising sodium hexafluoroacetylacetonate (Na(hfa)) and hexane, and
  - b) reacting the mixture for a time sufficient to etch and passivate the surface.
2. The process claim 1 wherein the metallic particles are aluminum.
3. The process of claim 2 further comprising evaporating hexane from the reaction mixture after reacting the mixture and then removing unreacted Na(hfa) by sublimation.
4. The process of claim 3 wherein sublimation is about 200°C and  $10^{-3}$  torr.
5. The process of claim 1 wherein the metallic particles comprise nanoparticles in the nanometer range of less than 10nm.

#### Patentansprüche

1. Verfahren zum Ätzen der Korrosionsschicht von der Oberfläche von Metallpartikeln und zur damit einhergehenden Bildung einer Passivierungsschicht, welches Folgendes aufweist:
  - a) Bildung einer Reaktionsmischung durch Dispersion von Natrium-Hexafluoracetylacetonat und Metallpartikeln mit Oxyd- oder Hydroxyd-korrosionsschichten in einer Lösung, die Natrium-Hexafluoracetylacetonat (Na(hfa)) und Hexan aufweist, und
  - b) Reaktion der Mischung für eine ausreichende Zeit zum Ätzen und Passivieren der Oberfläche.
2. Verfahren nach Anspruch 1, wobei die Metallpartikel Aluminium sind.
3. Verfahren nach Anspruch 2, welches weiter das Verdampfen von Hexan aus der Reaktionsmischung nach der Reaktion der Mischung aufweist, und dann die Entfernung von nicht reagiertem Na(hfa) durch Sublimation.
4. Verfahren nach Anspruch 3, wobei die Sublimation bei ungefähr 200 Grad Celsius und  $10^{-3}$  torr ist.

5. Verfahren nach Anspruch 1, wobei die Metallpartikel Nanopartikel im Nanometerbereich von weniger als 10 nm aufweisen.

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## Revendications

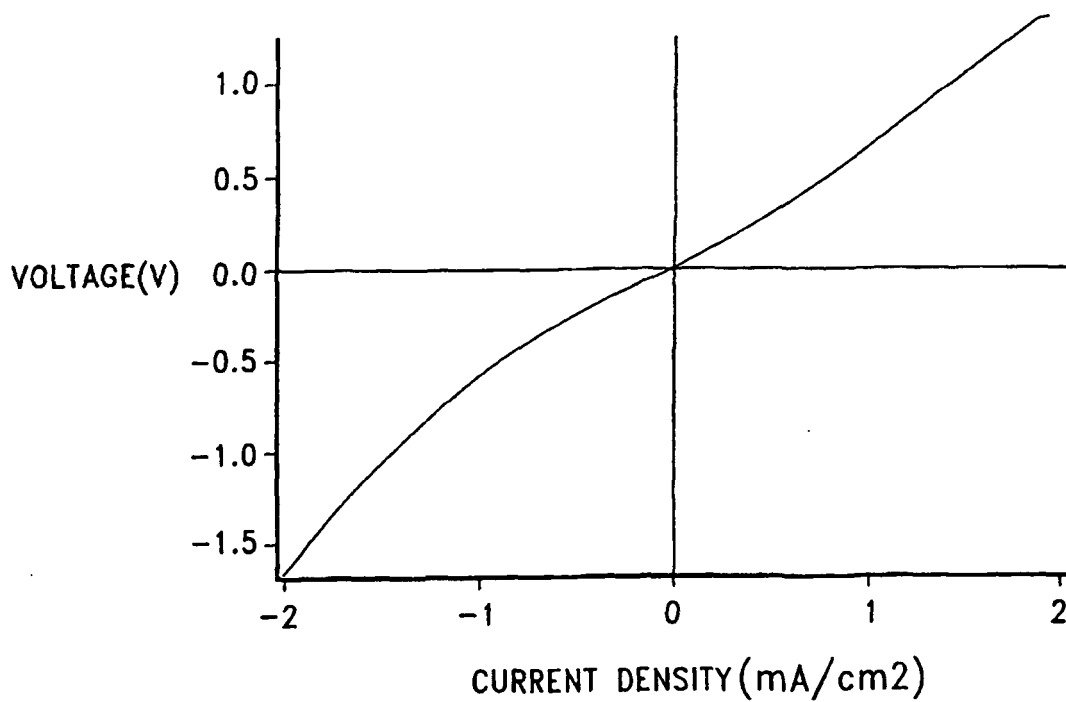
1. Procédé de gravure de la couche de corrosion et de formation concomitante d'une couche de passivation sur la surface de particules métalliques comprenant :
  - a) former un mélange réactif en dispersant de l'hexa-fluoroacétylacétonate de sodium et des particules métalliques comportant des couches de corrosion d'oxyde et d'hydroxyde dans une solution comprenant de l'hexa-fluoroacétylacétonate de sodium (Na(hfa)) et de l'hexane ; et
    - b) faire réagir le mélange pendant une durée suffisante pour graver et passiver la surface.
2. Procédé selon la revendication 1, dans lequel les particules métalliques sont de l'aluminium.
3. Procédé selon la revendication 2, comprenant en outre l'évaporation d'hexane du mélange de réaction après réaction du mélange et ensuite enlèvement du (Na(hfa)) n'ayant pas réagi par sublimation.
4. Procédé selon la revendication 3, dans lequel la sublimation s'opère à environ 200°C et  $10^{-3}$  torr.
5. Procédé selon la revendication 1, dans lequel les particules métalliques comprennent des nanoparticules dans la plage nanométrique inférieure à 10 nm.

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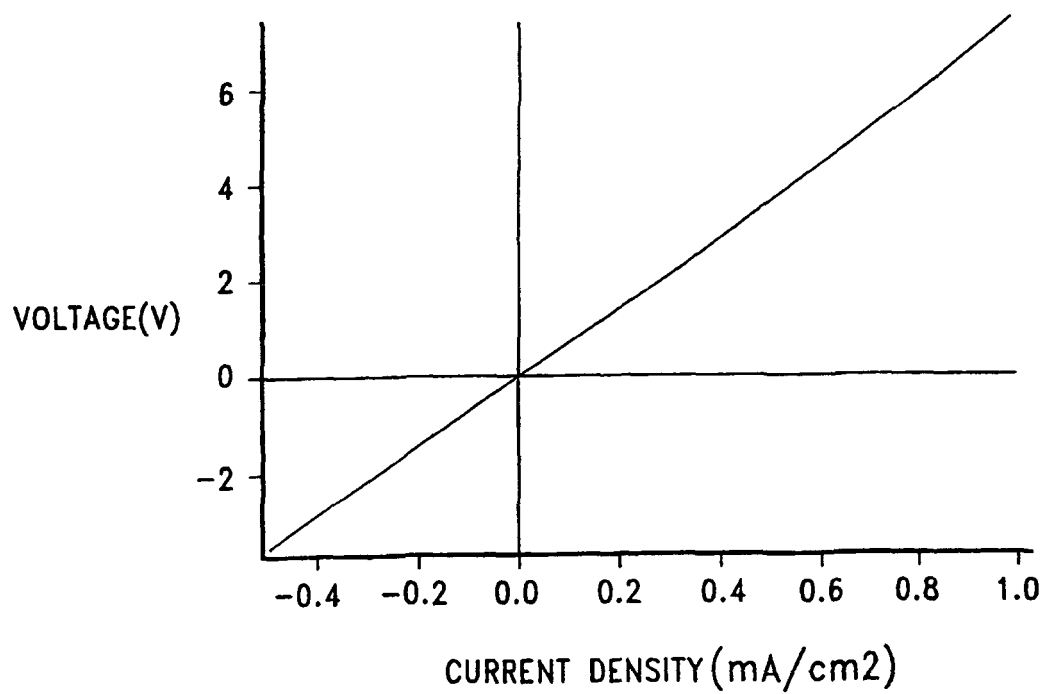
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*FIG. 1*



*FIG. 2*