PROPERTIES OF AMORPHOUS SEMICONDUCTING THIN FILMS

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1. Introduction

Amorphous semiconducting bulk and thin film materials have become the subject of intensive investigations during the last fifteen years. Their application is of increasing importance in various fields of physics and electronics. The aim of this work is to describe some basic characteristics of amorphous semiconducting films (ASF) as well as to show their application to switching and solar cells.

2. Classification of amorphous semiconducting materials

According to Ovshinsky and Fritzsche /1/, amorphous semiconductors can be divided into three groups.

The first and most important group consists of covalent amorphous semiconductors, which are divided into three subgroups:

a) tetrahedral amorphous films (as for example, Si, Ge, SiC, InSb, GaAs,...);

b) tetrahedral glasses of the type $A^{II}B^{IV}_xC^{V}_2$ ($CdGe_xAs_2$, $ZnSn_xP_2$, etc are the examples);

c) chalcogenides: elements and compounds (S, Se, Te, As_2S_3, As_2Se_3,...) as well as cross-linked network amorphous solids (Se-Te-As-Si, As_2Se_3-As_2Te_3, etc).

The second group comprises semiconducting oxide glasses (V_2O_5-P_2O_5, MnO-Al_2O_3-SiO_2, TiO_2-B_2O_3-BaO,...).

Dielectric films belong to the third group (SiO_x, Al_2O_3, ZrO_2, Ta_2O_3, BN, etc).

3. Preparation

ASF can be prepared in different ways. Vacuum evaporation on substrates at sufficiently low temperatures is used on a large scale. This method enables one to produce amorphous films of a number of elements, like germanium, silicon, selenium, tellurium, boron and arsenic, and of semiconducting compounds, such as InSb, GaSb, SnTe, PbTe, GeTe, InSe, In_2Se_3, As_2Se_3 or As_2Te_3. D.c. or r.f. cathodic sputtering and electrolysis are also used for producing amorphous films. Decomposition of a gaseous compounds in an electric discharge is used to obtain one of the components in the form of a thin amorphous film. A well-known example is decomposition of gaseous silane, SiH_4, in an electric discharge; amorphous silicon thus obtained is deposited onto appropriate substrates.

4. Structure

In a macroscopic sense, ASF in general and vacuum-deposited ASF in particular are isotropic, homogeneous and have very smooth surfaces. Nevertheless, deposition on less cold, less smooth or even impure surfaces and subsequent annealing can provide rough, discontinuous and partially crystallized amorphous films. In general, crystallization is impeded in vacuum deposition by low mobility of impinging atoms over the surface of the substrate. On the other hand, crystallization of amorphous films can be induced by light, electric field or laser pulse. The density of ASF is a few percent less than the density of the corresponding crystalline films.

The microstructure of ASF is characterized by loss of long-range order and by maintenance of short-range order extending over a distance of 1 to 2nm /2/.
The numbers and spatial arrangement of nearest neighbours correspond to those of one of the crystalline forms of the same element or compound.

The short-range order of an amorphous structure is of great interest and therefore we want to describe it as precisely as possible.

Three different approaches have been used to describe the short-range order of amorphous semiconductors:

- The microcrystal approach: it is assumed that perfect order reigns over a small distance, followed by an abrupt change in orientation of the next ordered domain;
- The perturbed-crystal approach: it is assumed that a large number of more or less conventional structural defects are frozen into an ideal crystal;
- The continuous-network approach: it is assumed that there are no discontinuites within the amorphous phase, its atoms forming a three-dimensional array of continuously interconnected atoms.

All these approaches are compatible with the general features of diffraction patterns of amorphous semiconductors.

Direct information about short-range order can be obtained by means of an extended X-ray absorption fine structure (EXAFS), However, three-dimensional short-range order cannot be obtained from the diffraction pattern or EXAFS analysis of amorphous material, but some structural model proposed could or could not agree with these analyses. Therefore, the only way of describing three-dimensional short-range order in amorphous semiconductors is to construct structural models.

5. Electronic properties of ASF

Energy-band structure. An energy-band model of an ideal crystal changes considerably when passing from this (ideal) structure to an amorphous one. According to the energy-band model given by Mott /3/, the transition from perfect order to increasing disorder causes the following modifications in density of electron states: the forbidden gap becomes narrower and localized states appear near its edges. The conductivity band and the valence band protrude their tails into the forbidden energy gap (Fig.1a). Electrons in localized states will be able to jump from one localized state to another if additional energy is applied; in this way, they can take part in the conduction process.

This process is called "hopping conduction". The energies E_c and E_v are no longer energies at which the density of electron states becomes zero; instead, these energies separate the region of localized states from the region of continuous (extended) states. Carrier mobility changes abruptly at these energies, and therefore they are called mobility edges.

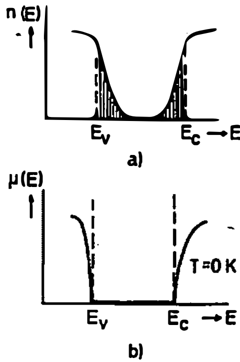

Fig. 1. The simplest band model for an amorphous semiconductor: a) density of states vs energy, n(E), b) carrier mobility vs energy.

The E_c-E_v interval is now called the forbidden mobility gap and not the forbidden energy gap (Fig. 1b).

The energy-band model mentioned above is related to an ideal amorphous structure with perfect short-range order and without long-range order. Real samples are, however, far from this ideal case. The density of tetrahedral amorphous films is, for example, by 15% less than that of the corresponding crystals, which indicates the presence of voids in the structure. Unsaturated bonds, vacancies and other defects are also present. All these irregularities cause increase in disorder and broadening of the tails of the valence band and of the conductivity band, so that they can overlap. This has led to the model of Cohen, Fritzsche and Ovshinsky (the CFO model) [4]. Other models have also been developed in order to interpret various properties of a large number of amorphous semiconductors. One of them is the model of Davis and Mott [5]. In their model, localized states related to long-range disorder are extended to some characteristic energies E_A and E_B; defects introduce narrow band of localized states near the centre of the forbidden gap (Fig. 2). Using this model, Davis and Mott tried to explain better the optical and electrical properties of amorphous semiconductors and ASF.

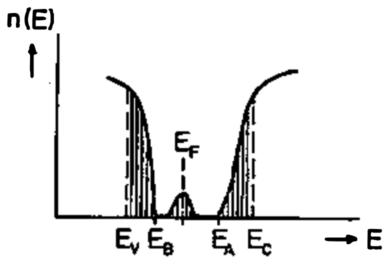

Fig.2. Density of states. n(E), according to Davis and Mott /5/

Transport properties. Three different mechanisms govern electrical transport in ASF. Assuming the Davis-Mott model, one distinguishes three principal contributions to conductivity /6/:

- at high temperatures, the predominant mechanism is conduction related to excitation of electrons into the conductivity band above E_c;
- at intermediate temperatures, the main contribution to the conduction process comes from the excitation of electrons into localized states near energy E_A (Fig.2). This is called hopping conduction or thermal tunnelling;
- at low temperatures, hopping conduction predominates througn levels in the vicinity of the Fermi energy. With decreasing temperature, the number and energy of phonons available for absorption decrease, so that tunnelling is restricted to seek centres which are not nearest neighbours. For this so-called variable-range hopping process, Mott derived the relation /7/

$$\sigma = \text{const.}\ \exp\left[-(T_o/T)^{1/4}\right].$$

Ambegaokar, Halperin and Langer /8/ found for T_o

$$T_o = \frac{16\alpha^3}{k \cdot n\,(E_F)} \quad ,$$

where α, the coefficient of exponential decay of localized state wavefunctions, was assumed to be independent of E. The quantity $n(E_F)$ is the density of states near the Fermi level. Expression is valid for low temperatures /9/. The conduction mechanisms mentioned above at high, intermediate and low temperatures have been established experimentally; best agreement has been obtained for amorphous germanium /10,11/, where the corresponding activation energies have been determined.

6. Switching effects

High electric fields produce different effects when applied to different materials. In insulators, high electric fields lead to a destructive breakdown. In a number of materials, crystalline and amorphous, switching and negative electrical resistance effects have drawn particular attention because these phenomena can be non-destructive.

First experiments with switching effects were performed on ASF. Current-voltage characteristics measured on such a film placed between two metal electrodes were of different shape, depending on the nature of amorphous material, the method of measurement and the type of electrodes /12/. Fig.3a) shows threshold switching. The I-V characteristic has two branches, the high-resistivity or OFF branch and the low-resistivity or ON branch.

When the applied bias rises above the threshold voltage V_{th}, the transition from the OFF state to the ON state occurs. The original state is re-established wnen the current is lowered below some holding current V_h. Fig.3b) shows a memory--switching device with two stable states. The conducting ON state, established after switching by a setting current, remains stable even if the voltage is entirely removed. The OFF state can be re-establiched by a short current pulse of either polarity.

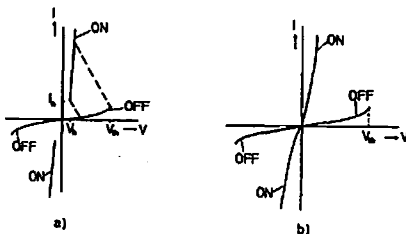

Fig.3. D.c. current-voltage characteristics in:
a) threshold switching;
b) memory switching.

A great deal of work has been devoted to the study of memory and threshold switching in different materials, especially in chalcogenide films /13-19/.

Memory switching appears in those materials in which reversible changes between two structural states occur; threshold switching, however is related to structure-stable materials. Changes between two structural states can also be induced by light, this is called optical switching /20/. Optical switching appears in the same materials in which electrical memory switching occurs.

Any system which can be brought from some initial state to some final state must be activated to overcome the energetic barrier which keeps the states in stable or metastable equilibrium. This activation barrier can be reduced or overcome by an electric field, an electric pulse, light, heat, etc. A change in physical structure may involve long-range order; for example, in a transition from an amorphous to a microcrystalline state in the case of memory switching in an electric field /21/, or it may be limited to the local arrangement of atoms; for example, in a photostructural process, photopolymerization and the photodarkening effect /22-24/. A change in physical structure may also effect the homogeneity or the chemical composition of the amorphous material; for example, light-induced phase separation /25/ and photodoping /26/. Some of these effects can be made reversible, and then they can be applied to information storage and control.

7. Application of thin amorphous silicon films to solar cells

Utilization of amorphous silicon as solar-cell material has recently received considerable attention. It has been found that amorphous Si films could be obtained by applying the r.f. glow discharge in silane (SiH_4) /27/.

These films have stable electrical characteristics and can be n- or p-type doped by addition of phosphine (PH_3) or diborane (B_2H_6) to silane. This process causes the formation of large-area solar cells. Paul et al.[28] have shown that amorphous silicon can be p- or n-type doped by r.f. sputtering under hydrogen partial pressure, similarly as in the glow discharge.

Favourable properties of amorphous Si are the following: high absorption coefficient and optimum band gap [29], n-type and p-type doping [30], realization of Schottky barriers [31] and p-n junctions[32]. The maximum conversion efficiency reported up to now is 5.5%, a value measured on a Schottky-type photovoltaic structure[33]. The theoretical limit of conversion efficiency has been estimated to be 15%, assuming a collection efficiency of 100% in a film 1 µm thick[27].

In order to achieve high-efficiency solar cells, amorphous Si grown under r.f. sputtering has been n-doped using gaseous nitrogen as a dopant. Addition of nitrogen increases the photoconductivity of the doped material over that of the undoped material[34].

To increase the conversion efficiency, it would be desirable to use amorphous Si_xGe_{1-x} alloys for making stacked multijunction structures. The cascade arrangement of several junctions would allow one to increase the overall collection efficiency with respect to a single junction [35].

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