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Thin film Si:Eu and Si:Y composites

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The composition, electrical, and optical properties of silicon film composites doped with rare-earth elements have been studied. The effect of the deposition temperature, the substrate type on the film properties has been determined. The materials have been shown to be of interest for thin film photoresistors, photodiodes, UV radiation sensors, and photoelectric converters.

Исследованы состав, химические и оптические свойства пленок кремниевых композитов с примесями редкоземельных элементов. Определено влияние температуры осаждения и типа подложки на свойства пленок. Показано, что данные материалы могут представить интерес для создания тонкопленочных фоторезисторов, фотодиодов, датчиков УФ излучения и фотоэлектрических преобразователей.

1. Introduction

Silicon doped with rare-earth elements (RE) attracts more and more attention as a material of very good promises for optoelectronics. Most of published works is aimed at studies of Er dopant providing the photoluminescence in such structures at 1.54 μm wavelength which provides minimum loss in fiber-optic communication lines [1, 2]. The properties of silicon films doped with other RE are studied to a considerably lower extent. In particular, europium and yttrium application is rather prospective with respect to improved sensitivity of silicon material to VIS and UV radiation and also to efficiency of solar cells [3, 4].

The synthesis of thin-film Si:Eu and Si:Y composites is somewhat limited. For example, those materials cannot be obtained by chemical methods, because REs do not form gaseous compounds. That is why physical methods such as magnetron sputtering [5, 6] and electron-beam evaporation [7] are used. Moreover, low solubility of rare-earth elements in crystalline matrix is known, while amorphous silicon enables to increase considerably the content of those dopants in films. A peculiarity of silicon films with Eu dopants is due to its variable valency (+2 and +3). Europium atoms in a silicon film have been shown to be in both valent states [6] that implies the formation of two impurity center types, electrically inactive and donor type, conversion from one to another type being defined by the substrate temperature. Moreover, the photosensitivity of silicon material is known to increase considerably due to incorporation of Eu [5] and Y [7] dopants. However, the published investigation results of thin-film composites Si:Eu and Si:Y [5–7] concerned mainly properties of the films without examination of barrier structures based thereon.

Before, we have synthesized Si:Eu films of different quantitative composition (95:5 and 67:33 at.%) using the electron-beam evaporation [8]. It has been shown that europium has a rather high solubility level in silicon film (10–30 at.%) even if its content in the initial alloy is as low as 5 at.%. The films deposited from alloy with high Eu concentration were found to be unusable because of their rapid oxidizing in air. The films deposited from the Si:Eu 95:5 at.% alloy were studied in more detail. A bilayer structure of Si:Eu film was revealed, the bottom layer being situated at the film/substrate boundary and characterized by high content of Eu and unintended dopants. The same result was obtained for Si:Er films in [1]. The study of the dopant center nature has been shown two types of Eu including centers of different valences that coordinate with results in [6].

The aim of this work is to study the properties of silicon films with europium and yttrium dopants. Furthermore, the use of yttrium is due to possibility to get more reproducible chemical composition of the film relative to the initial alloy because of almost the same saturated vapor pressure of silicon and yttrium that is of importance in the film deposition using the electron beam evaporation.

2. Experimental

Thin silicon films were deposited onto dielectric substrates SiO_2 to study the film properties and onto semiconducting *p*-Si and *n*-Si to prepare heterostructures. The technological parameters of films deposition were as follows: pressure of residual gases 10^{-5} Torr, deposition time 5 min, substrate temperature 100 to 350°C. The ohmic contacts were formed by deposition of Ti–Ni bilayer of 30 and 350 nm thickness, respectively, using the electron-beam evaporation

The RE dopants were introduced from specially prepared initial Si:RE alloys obtained by arc-heating in argon atmosphere with previous titanium sputtering in vacuum chamber. The following initial alloys were used: 1) Si:Eu — 95:5 at.%; 2) Si:Y — 90:10 at.%; 3) Si:Y — 67:33 at.%. The pure silicon films were obtained in the same technological conditions to compare the effects of different RE dopants. The chemical composition of the samples was examined by Auger spectroscopy using a LAS-2000 Riber. To study the element distribution over the film depth, the sample surface was bombed with argon ions of 4 keV energy. The etching rate was 30 A/min. To measure the sensitivity to ultraviolet radiation, a UV-lamp with 350 nm wavelength was used.

3. Results and discussion

The samples so obtained have the following structure in cross section: contacts of 30 nm thickness (only the lower layer (Ti) is shown in the spectrum), 5 to 40 nm thick silicon film and substrate (oxidized silicon layer) of 20–30 nm thickness on *c*-Si (Fig. 1, a) or *c*-Si (Fig. 1, b, c). The film consists mainly of Si and intentional dopants — europium (Fig. 1, a) or yttrium (Fig. 1, b, c), and also contains a certain amount of unintentional dopants (O, C, SiO_2). As to Y dopant, the reproducibility of chemical composition with respect to the initial alloy is observed. That is, the films deposited from Si:Y 67:33 at.% alloy contain 30–35 at.% of yttrium (Fig. 1,c), while those obtained from Si:Y 90:10 at.% alloy contain 3–5 at.% of this dopant (Fig. 1, b). For comparison, europium enters the silicon film at a level of 20–30 at. % while its content in the initial alloy was only 5 at.% (Fig. 1, a). The Y distribution over the film depth is inhomogeneous and not the same at its different

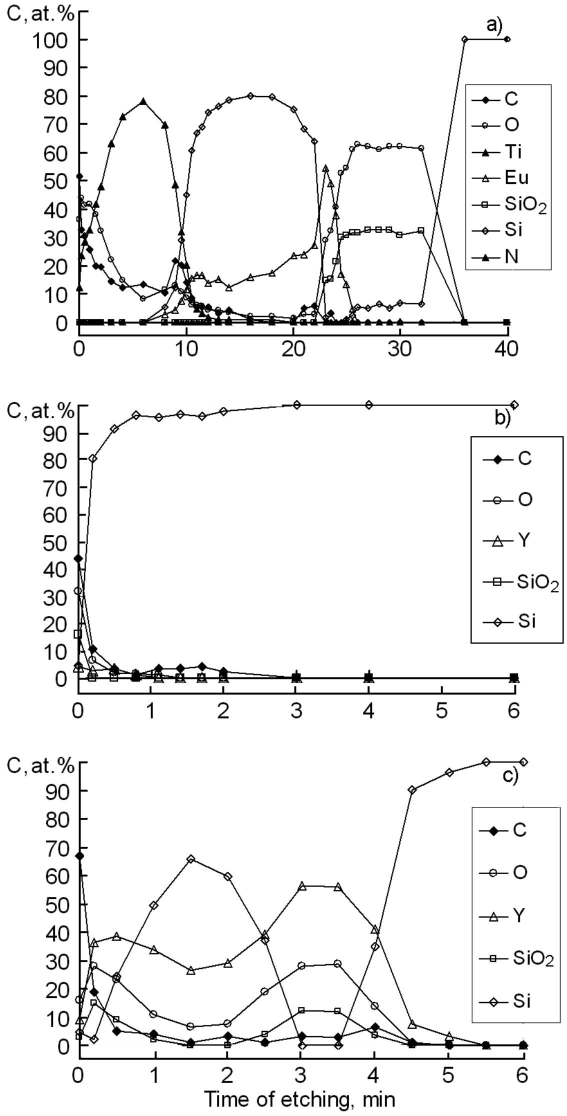

Fig. 1. Chemical compositon profiles over the depth of films deposited from alloys: Si:Eu — 95:5 at.% (a); Si:Y — 90:10 at.% (b); Si:Y — 67:33 at.% (c).

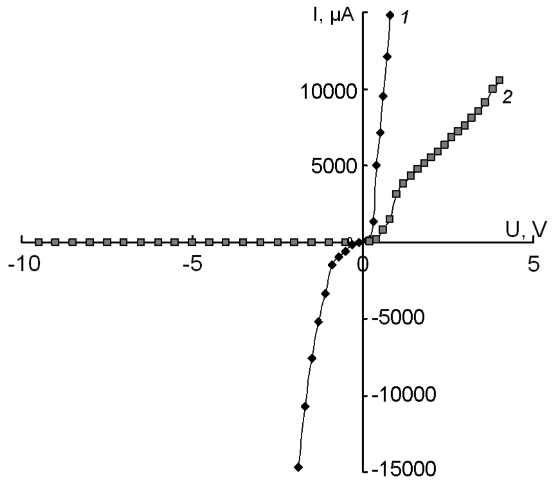

Fig. 2. *I-V* characteristics of the iso- and anisotype heterostructures. *1* – *n*-Si; *2* – *p*-Si.

concentrations. For samples with Y content of 30 at.%, the maximum dopant concentration is observed at the film/substrate interface (Fig. 1, c) while for films with low yttrium concentration, its content decreases gradually towards the substrate (Fig. 1, b).

The data of Auger spectroscopy enable to suggest the formation of a bilayer film in the case of high rare-earth concentration. The lower layer in contact with the substrate is characterized by a high content of RE and unintentional dopants. The thickness of such a transition layer makes 1 to 10 nm. In the second layer, the RE concentration is low. That result can be explained as follows. It is known that, in contrast to chemical compounds, the components of an alloy evaporate independently. The evaporation rate of Si, Y and Eu can be estimated [9] as

$$v_{evap} = 6 \cdot 10^{-4} \cdot \left(\frac{M}{T_{evap}}\right)^{1/2}, \tag{1}$$

where v_{evap} is the evaporation rate; M, the molecular weight; T_{evap}, the vaporization temperature. According to formula (1), v_{evap} for Si, Eu, Y make up $0.7{\cdot}10^{-4}$, $2.5{\cdot}10^{-4}$ and $1.3{\cdot}10^{-4}$ g/cm$^2{\cdot}$s, respectively. That is, at first, the high-volatile component (Eu/Y) is evaporated and then Si. Thus the films are of sandwich type. The Eu concentration in silicon films deposited from alloy with content of this dopant only 5 at% reaches the same value as in the samples obtained from Si:Y 67:33 at% alloy. The spectra represented in Fig. 1 demonstrate also the getter properties of Eu and Y in high concentrations. A similarity of dopant distribution for RE element and oxygen is clearly traced that can be an evidence for RE-O bond.

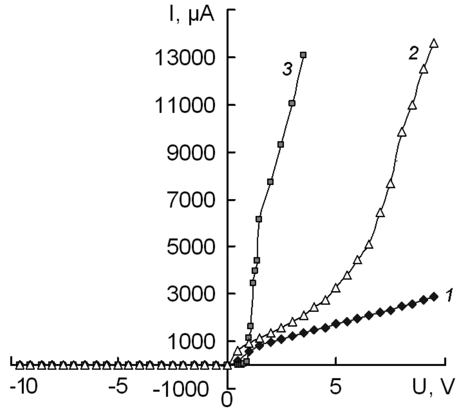

Fig. 3. Influence of Y introduction on *I-V* characteristics of the heterostructure. *1* – Si; *2* – Si:Y (67:33 at.%); *3* – Si:Y (90:10 at.%).

The introduction of RE dopants causes considerable changes in electric conductivity of the films. The dark current in Eu-doped film is about three orders of magnitude greater than in undoped one. The introduction of Y favors also the current increase. Moreover, this increrase is in parallel with the Y content in the initial alloy. So, introduction of 10 and 33 at% of yttrium result in growth of electrical conductivity by about one and two orders of magnitude, respectively. The difference in the influence of these RE can be caused by higher reactivity of Eu.

The formation of anisotype and isotype heterojunction on the *p*- and *n*-Si substrates, respectively, is to note first of all (Fig. 2). The isotype heterojunctions are seen to be characterized by the presence of double saturation that results in deterioration of rectifying properties. The anisotype heterostructures demonstrate the rectification factor at the level of 700 under 1V. The electrical properties of heterojunctions also undergo considerable changes when RE dopants are introduced. But, in contrast to films, the electrical characteristics of heterostructures are deteriorated as a rule. Moreover, there is a difference in influence of europium and yttrium on isotype and anisotype heterojunctions. The current-voltage characteristics (IVC) of heterostructures based on Si:Eu films are characterized by lower rectifying properties as compared to structures without RE dopants. The introduction of Y into films deposited on *p*-Si substrates does not result in well-defined

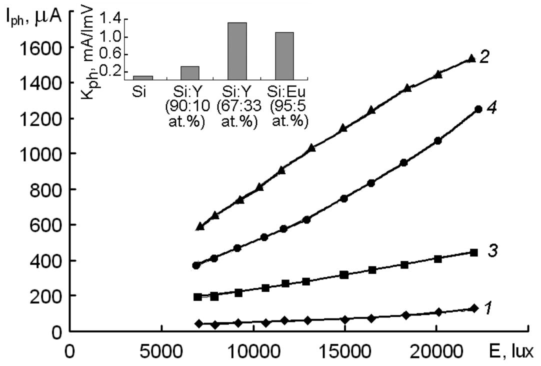

Fig. 4. Influence of RE introduction on current-illumination characteristics of the films. *1*, Si; *2*, Si:Y — 67:33 at.%; *3*, Si:Y — 90:10 at.%; *4*, Si:Eu — 95:5 at.%. The inset is the comparative diagram of photosensitivity coefficients of the films.

deterioration of (*I-V*) curves. At increased deposition temperatures (>200°C), the IVC demonstrate a more distinct rectifying than structures without the impurities (Fig. 3).

Using the obtained films, photoreceivers of resistive and diode type were realized. The current-illumination characteristics (LAC) were measured (Figs. 4, 5) and the photosensitivity coefficients were calculated as

$$K_{ph} = \frac{I_{ph2} - I_{ph1}}{(\Phi_2 - \Phi_1) \cdot U} = \frac{I_{ph2} - I_{ph1}}{(E_2 - E_1) \cdot S \cdot U}, \quad (2)$$

where K_{ph} is the photosensitivity coefficient; I_{ph}, photocurrent; Φ, the light flux; E, illumination; S, the sample area; U, the LAC measurement voltage.

All samples demonstrate the sensitivity to visible light that was revealed as the photocurrent appearance under illumination. The sensitivity values depend on the deposition temperature, the RE presence and type. An improvement in photosensitive properties is observed at elevated deposition temperatures, while electric conductivity undergoes the minimum influence of RE. This can be related with specific features of a dopant introduction into silicon matrix. Namely: at low deposition temperatures (<200°C), the RE impurities show more getter properties, but in the high temperature range (>200°C) those dopants act as traps for minority carriers. The films with Y dopant are characterized by photosensitivity increased coefficient as compared to the Eu doped ones (inset in Fig. 4).

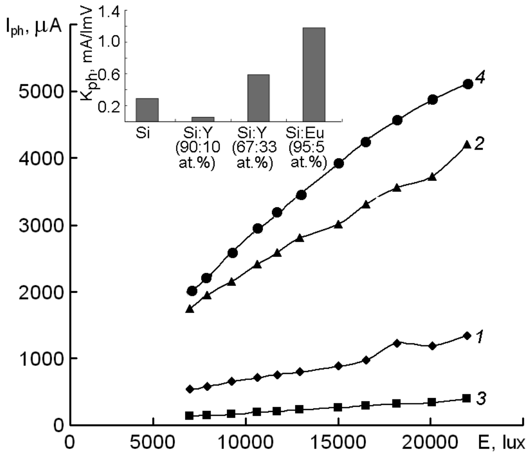

Fig. 5. Influence of RE introduction on current-illumination characteristics of a heterostructure. The curves are numbered as in Fig. 4.

The coefficient of UV sensitivity is calculated as (3):

$$K_{ph} = \frac{I_{ph}}{P}, \quad (3)$$

where K_{ph} is the UV sensitivity coefficient; P, the light flux rate.

The properties of a heterojunction are defined mainly not by the film properties but by quality of the film/substrate boundary. The fact, that character of Eu and Y influence on electrical and optical properties of heterostructures are the same is an evidence of this statement. As well as for dark current, a decrease of photocurrent under introduction of RE impurities (Eu, Y) is observed in isotype heterostructure, but for anisotype ones, improved optical properties take place at certain deposition temperatures (Fig. 5). The europium dopant provides a more influence on UV sensitivity of a heterojunction than yttrium, that can be explained by the specific structure of Eu energy levels, allowing to absorb UV radiation more efficiently than Y.

In valve regime of photodiode, the value of open circuit voltage (V_{oc}) was measured. The isotype structures do not demonstrate photoelectric effect, regardless of preparation conditions and chemical composition, while anisotype heterojunctions reveal the open circuit voltages of 120 to 400 mV. Such distinction is explained obviously by forming of a rather high barrier at the film/substrate boundary in anisotype heterojunctions. The incorporation of RE impurities at the rate of about 30 at.% at

100–200°C deposition temperatures results in an increased V_{oc}. So, maximum values of open circuit voltage in thin film photoelectric converters on the base of pure silicon films (250–300 mV) can be improve by introducing europium (380 mV) or yttrium (400 mV).

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Тонкоплівкові кремнієві композити, леговані європієм та ітрієм

В.М.Коваль, Ю.С.Чечуга

Досліджено склад, хімічні та оптичні властивості плівок кремнієвих композитів з домішками рідкісноземельних елементів. Визначено вплив температури осадження та типу підкладки на властивості плівок. Показано, що ці матеріали можуть становити інтерес для створення тонкоплівкових фоторезисторів, фотодіодів, сенсорів УФ випромінювання та фотоелектричних перетворювачів.