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OPTICAL PROPERTIES OF a-Si:H DEPOSITED BY HOMOGENEOUS CVD METHOD

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Abstract. The optical properties of a-Si:H films deposited by homogeneous CVD method are examined depending on the substrate temperature T_s. The optical parameters are calculated by the transmission spectrum taking into account the nonhomogeneity of the films. A deviation from the linearity has been observed in the dependence of the optical band gap E_g on the substrate temperature. The refractive index and coefficient B, determined from the Tauc correlation, are not monotonous functions of E_g. This behavior is connected with the peculiarities of the deposition method.

Резюме. Исследованы оптические свойства пленок a-Si:H, полученных гомогенным CVD методом, в зависимости от температуры подложек T_s. Из трансмиссионных спектров определены оптические параметры, учитывая негомогенности пленок. Зависимость ширины оптической запрещенной зоны от температуры роста отклоняется от линейной. С изменением E_g показатель персломления и коэффициент B из соотношения Тауца изменяются немонотонно, что связывается с особенностями метода получения.

1. Introduction

The unusual interest in the hydrogenated amorphous silicon (a-Si:H) and its electronic and solar energy applications provoke a fast development of deposition technology. Together with the wide spread method of glow discharge, different modifications of chemical vapor deposition (CVD) have been developed, one of which is the homogeneous CVD method [1]. The advantages of this method, as well as the reached high growth rates [2], make the method interesting for practical application. Films characteristics are very sensitive to the technological conditions — gas temperature, mass flow rate of silane (SiH_4), pressure and substrate temperature. The object of this work is the investigation of the optical characteristics depending on the substrate temperature in an wide interval. The substrate temperature is an important factor, which governs the microscopic structure of the material and the configuration of silicon-hydrogen bonding.

2. Experiments

The undoped films a-Si:H are grown by the homogeneous CVD method in the following conditions: gas temperature — 660°C, silane mass flow rate — 60–80 sccm, pressure in the reactor — 130 Pa. The growth temperature (substrate temperature) T_s is from 150° to 370°C. Pure electronic grade silane (100% SiH_4) is used. The films are deposited on quartz, sodium glass or corning 7059. Film thickness is from 0.4 to 1.3 μm. Deposition rate is from 3 to 5 nm/min. The arrangement of the reactor and the study of the growth conditions in detail will be published in this journal later.

Only data from the transmission spectrum are used for determination of the optical parameters thickness d, nonhomogeneity $\Delta d(\lambda)$, refractive index $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$. The transmission spectrum of the films is measured in the range 200–2500 nm with spectrophotometer Perkin-Elmer 330 with wavelength accuracy ± 0.2 nm for UV and VIS, and ± 1 nm for NIR region. Photometric accuracy is $\pm 0.3\%$ T.

Nonhomogeneity Δd is a summarized parameter, showing the variations of film thickness, the variations of refractive index and absorption coefficient along the depth and area of the film. The more homogeneous and perfect the film, the smaller d.

A programme for computing and graphic representation of optical characteristics as a function of photon energy is developed following the method for determining the optical constants proposed by Swanepool [3, 4]. This method proposes an important simplification: $T_{\min}$ and $T_{\max}$ are considered as continuous functions of λ through $n(\lambda)$ and $\alpha(\lambda)$. These functions are the envelope of the maxima $T_{\max}(\lambda)$ and the minima $T_{\min}(\lambda)$ in the transmission spectrum.

The optical processes are considered at the boundary air-film, film-substrate, substrate-air. The refractive index of substrates is taken as an input programme parameter.

Three ranges of the transmission spectrum are discussed. The first is characterized by a small absorption, which can be neglected. With iterative steps $n(\lambda)$ and $\Delta d(\lambda)$ are determined. In the second range the absorption participates in the calculations. It is assumed that the nonhomogeneity has a constant value ($\Delta d = \lim \Delta d$, $n \to \infty$). $n(\lambda)$ and $\alpha(\lambda)$ are determined by iterative steps. In the third range a strong absorption is observed. The value of Δd is assumed zero. The refractive index is determined by an exploration of the values received in the other two ranges. The absorption coefficient is computed for the homogeneous film.

The admitted errors in the calculation of the optical characteristics are determined by accuracy of the spectrophotometer, by the accuracy of the computer programme, by the subject participation in the spectrum envelopes procedures and the dividing of the spectrum into three ranges. The reached accuracy is truly enough for a qualitative and a quantitative estimate of the film. For example, the difference between the computed optical film thickness and the measured one by the stylus method by Taylistep is lower than 5–7 % d.

3. Results and Discussion

The spectral dependence of the absorption coefficient for some of the films at different substrate temperatures is shown in Fig. 1. The absorption coefficient increases with the increasing of the photon energy, and the relation between them is given by Tauc ratio [5]:

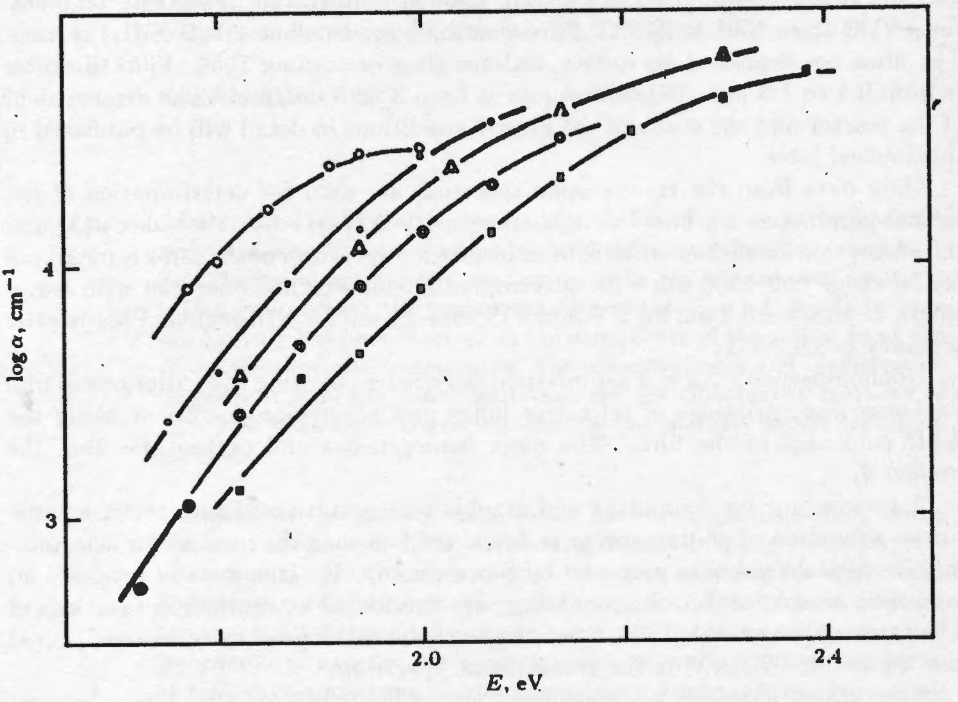

Fig. 1. Spectral dependence of absorption coefficient of the thin films a-Si:H, deposited at different temperatures of substrates T_s: *1* — $T_s = 240°C$; *2* — $T_s = 258°C$; *3* — $T_s = 296°C$; *4* — $T_s = 308°C$; *5* — $T_s = 362°C$

$$\sqrt{n\alpha h\nu} = B(h\nu - E_g).$$

The dependence of $\sqrt{n\alpha h\nu}$ on photon energy for some a-Si:H films, deposited at different temperatures is shown in Fig. 2. Neglecting the factor $n(h\nu)$ does not disturb the linearity of the ratio and it changes the value of E_g with less than 50 meV. The part that the extrapolated line cuts from the abscissa for $\alpha = 0$ is the optical band gap E_g.

The change of the band gap is connected with the including of hydrogen in the silicon network structure [6]. Dangling bonds are the main defects in a-Si (nonhydrogenated amorphous silicon). The included hydrogen saturates these bonds, the density of states decreases and the band gap increases. The correlation $E_g = 1.5 + 0.015c_h$ for glow discharge a-Si:H films is received, where c_h is

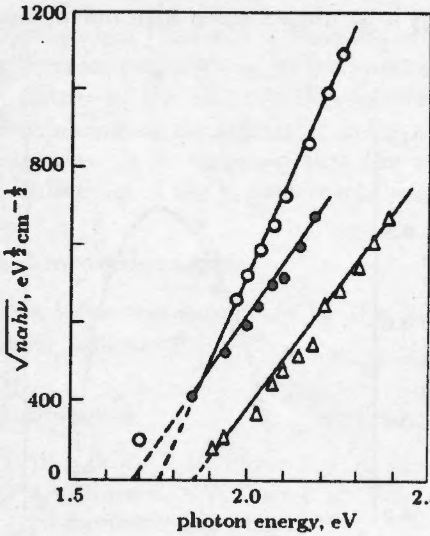

Fig. 2. Absorption coefficient in form proposed by Tauc [1] for samples deposited at different substrate temperatures T_s

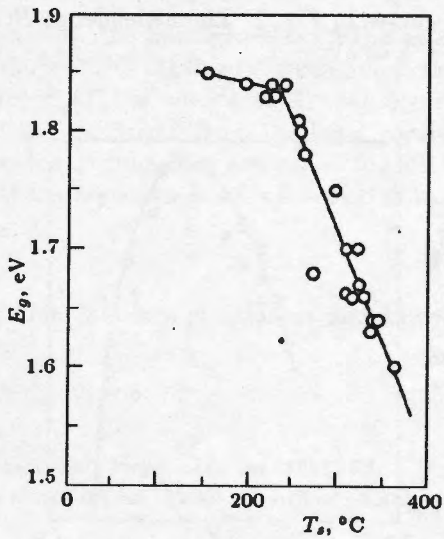

Fig. 3. Dependence of optical band gap E_g on the substrate temperture T_s

the concentration of hydrogen in at.%. The quantity of the included hydrogen decreases with the increase of temperature T_s, therefore the band gap decreases too. It is accepted that E_g depends linearly on T_s with a constant slope in the whole temperature interval.

The results of our study of a-Si:H films deposited by homogeneous CVD do not confirm these data. The dependence of E_g on substrate temperature T_s is shown in Fig. 3. With T_s decrease, E_g increases linearly, so for T_s from 360° to 240°C E_g increases from 1.6 to 1.84 eV. At temperatures 240°–250°C the slope changes and we may say, that E_g does not or depends slightly on T_s.

For CVD a-Si:H films, again deposited by thermal decomposition, but of bisilane Si_2H_6, such a behavior of $E_g(T_s)$ is published in [7]. The maximum observed at $T_s \sim$ 430°C. For glow discharge a-Si:H a similar curve is observed, but it depends on the annealing temperature [8]. This peculiarity is explained by the simultaneous action of two competitive processes — efusion of hydrogen and relaxation of structure network.

We suppose a few reasons for the nonmonotonous dependence $E_g(T_s)$ of the homogeneous CVD: (1) Hydrogen incorporation stops at low T_s; (2) E_g depends more directly on T_s than c_h, i.e. below some temperature E_g stops to increase while c_h continues to increase; (3) E_g does not depend on c_h, but on the structure of hydrogen-silicon bonding and on microstructure; (4) A self-annealing occurs during deposition. Unfortunately, there are no sufficient data to point out the reason.

The dependence of the coefficient B on the band gap is shown in Fig. 4. B is determined as a slope in correlation (1) on the range of the intrinsic transitions. It includes the average matrix element of the optical transition probability and it is connected with the form of the band tail. B is calculated as a square of $\mathrm{tg}(\gamma)$ for the curves in Fig. 2. The dependence $B(E_g)$ is nonmonotonous with maximum at $E_g \sim 1.75$ eV.

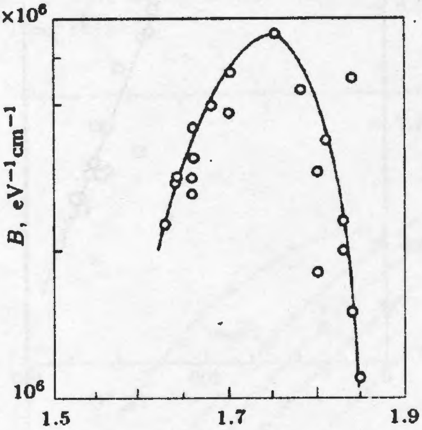

Fig. 4. Coefficient B as a function of optical band gap E_g

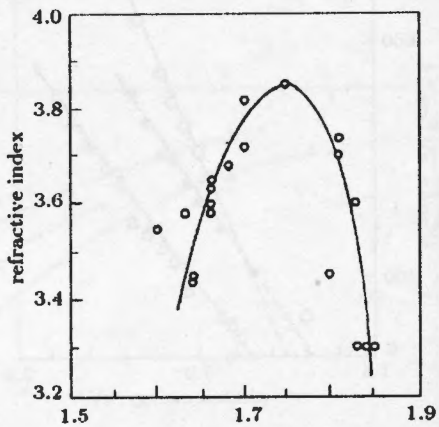

Fig. 5. Dependence of the refractive index at 2000 nm on the optical band gap

The same peculiarity — the maximum at 1.75 eV is observed in the refractive index dependence on E_g (Fig. 5). The values of n shown in the Figure are determined at 2000 nm where there is no absorption. We have to note that the refractive index for a-Si:H films obtained by homogeneous CVD method has values higher than those obtained by other methods.

Our data for B are in contradiction with the data published in [9] for the a-Si:H films received by sputtering. A monotonous increase of B with E_g is observed within the interval 1.4–2.0 eV. Such a behavior is connected with the prediction that the number of the states in the band tail is constant and with the increasing of E_g only a predistribution of these energy states is setting in.

As far as the properties of a-Si:H are strongly dependent on the deposition conditions, we can suppose that the films obtained by homogeneous CVD essentially differ from those obtained by sputtering and other methods. Now we accept the supposition of Scott [10]: a-Si:H films, grown at low T_s by homogeneous CVD contain much more hydrogen than the films grown by other methods. a-Si:H films, which can be considered random alloys with mostly Si:H bonding and mixtures of SiH and SiH_2 groups, become progressively less-linked at low T_s. Isolated SiH_2 groups form $(SiH_2)_n$ clusters, which create rings and chains of polysilane. The structural transition temperature is strongly dependent on the growth conditions.

4. Conclusions

The studied thin a-Si:H films are obtained by the homogeneous CVD method at substrate temperatures in the interval 150°–370°C. At low substrate temperatures a change of the slope in the dependence $E_g(T_s)$ is observed. A nonmonotonous dependence of the refractive index and the coefficient B on the band gap is also observed. It is supposed that the observed peculiarities are connected with the peculiarities of the growth mechanism of the homogeneous CVD a-Si:H films.

Acknowledgments

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