Functional Materials 8, No.2 (2001)

Ellipsometric studies of amorphous Ge films on single-crystalline GaAs substrates

V.A.Odarich, O.V.Rudenko, M.P.Semen'ko, R.V.Konakova, V.F.Mitin*, V.V.Kholevchuk**

T.Shevchenko Kyiv National University,
2 Glushkov Ave., 03127 Kyiv, Ukraine
*Institute of Semiconductor Physics, National Academy of Sciences
of Ukraine, 45 Nauki Ave., 03028 Kyiv, Ukraine

Received April 11, 2000

Multiangular ellipsometric examinations of amorphous germanium films have been carried out. The films were obtained by deposition in vacuum onto the semi-insulating single-crystalline GaAs (100) substrates. The multiangular ellipsometric measurements procedure is presented providing the determination of the reflecting system parameters. It is found that an oxide layer, 4 to 8 nm thick, is formed on the film surface. The refractive indices of this layer in the 313–579 nm spectral range and optical constants of the amorphous Ge film have been measured.

Проведены многоугловые эллипсометрические исследования аморфных пленок германия, полученных методом осаждения в вакууме на подложки из полуизолирующего монокристаллического GaAs (100). Изложена методика обработки многоугловых эллипсометрических измерений, которая позволяет найти параметры отражающей системы. Обнаружено, что на поверхности пленок образуется окисный слой толщиной от 4 до 8 нм. Измерены показатели преломления этого слоя в спектральной области 313–579 нм и оптические постоянные пленки аморфного германия.

The Ge/GaAs heterostructure is of interest for both fundamental investigations and practical applications. A number of devices have been developed on its basis, such as photodetectors [1–4], diodes [5, 6], temperature, strain and magnetic field sensors [7, 8]. A characteristic feature of the Ge/GaAs heterostructure is that the lattice constants of Ge and GaAs are close to each other. The relative difference between them is 0.08 %. In this respect, the above heteropair is ideal. Besides, the linear expansion coefficients for both materials are essentially the same over a wide temperature range. All the above facts provide favorable conditions for epitaxial growth of Ge films on GaAs substrates and enable to obtain both Ge films and heterojunctions of perfect structure.

The structural perfection degree as well as the structural defect concentration in Ge films obtained using evaporation in vacuum depends mainly on the temperature of GaAs substrate during film deposition. Single-crystalline Ge films on GaAs are obtained at temperatures over 450°C (in some cases, it may be 300°C). Even at low (200–300°C) substrate temperatures, Ge films are as a rule polycrystalline. Amorphous Ge films are obtained usually by deposition onto a substrate at a temperature close to room one. Many researchers have investigated the electrical and optical properties of amorphous Ge films on various substrates [9–15]. However, the amorphous Ge films on GaAs substrates have not been studied in essence. The properties of amorphous Ge are well known to depend essentially on the preparation technique and conditions as well as on the subsequent heat treatment [9].

This work deals with ellipsometric studies of amorphous Ge films on GaAs. Ellipsometry is highly sensitive to the sample properties in the near-surface region. It enables one to determine the structure and parameters of a system that is formed when depositing a semiconductor film onto a substrate. We determined the refractive and absorption indices for an amorphous germanium film as well as the refractive index and thickness of the oxide layer on this film.

The films were prepared using thermal evaporation of Ge in vacuum (at a pressure of $3\cdot10^{-4}$ Pa) onto substrates made of single-crystalline semi-insulating GaAs (100). The substrates were subjected to chemical dynamical polishing. Just before the film deposition, the substrates were etched to remove the damaged surface layer and held in vacuum (at a pressure of $3\cdot10^{-4}$ Pa) for one hour at a temperature of 550°C. During the film deposition, the substrate temperature was about 120°C. The film thickness, d, was 1.2 μm. The prepared samples were kept in air for a long time (several months).

The film structure and crystal lattice parameters were examined using electron diffractometry. Ellipsometric measurements were performed using a version [16] of Beattie photoelectric technique where the ellipsometric parameters, $\cos\Delta$ and $\mathrm{tg}\,\psi$, are measured, (Δ is the phase difference between the orthogonal projections of the electric vector of light wave; $\mathrm{tg}\,\psi$, the ratio between the reflection coefficients for these projections at a fixed angle of incidence). The measurements were performed at seven spectral lines of the mercury lamp emission in the 313–579 nm wavelength range, within a wide range of the probing beam incidence angle on the sample under study. The ellipsometer was calibrated using a silicon wafer with essentially time-constant optical properties due to a protective native oxide film on its surface. Before the measurements, the sample surface was etched for 3–10 min in 3–20 % water solution of hydrogen peroxide.

Electron diffractometry has shown that the films studied had an amorphous structure (Fig. 1a). Heating of samples at a temperature of 300±20°C in the instrument column resulted in the film crystallization, i.e., the amorphous phase transformed to polycrystalline one (Fig. 1b). Such a film consists predominantly of crystalline grains of several tens nm in size. The point reflections from large crystallites were observed, too.

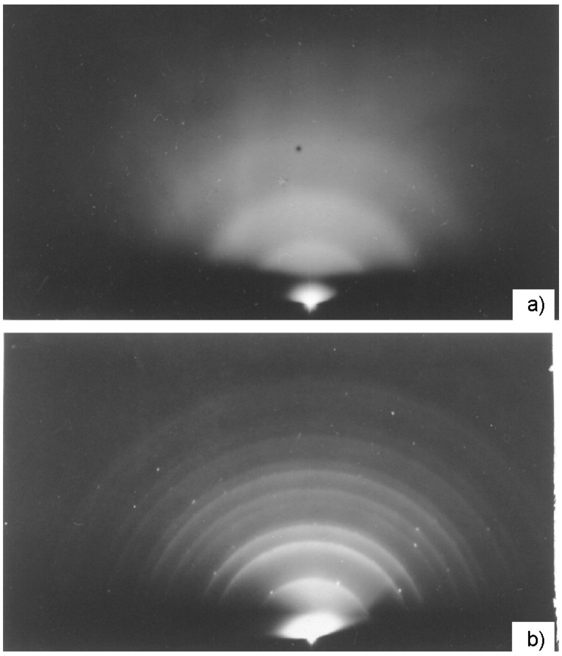

Fig. 1. Electron diffraction patterns of Ge films: *a* — initial; *b* — after thermal annealing at $T = 300\pm20$°C.

In Fig. 2 presented are the angle dependences of ellipsometric parameters obtained at two wavelengths from the spectral range studied. These dependences are monotonic. This evidences a considerable thickness of the outer surface layer, of the amorphous Ge film, so the probing light beam does not penetrate through the film to the GaAs substrate. In fact, the depth of the probing beam penetration into the film is about 20 nm only, due to high light absorption in Ge, while the Ge film thickness is 1.2 μm. Therefore the reflected light wave (that is analyzed in ellipsometric studies) is formed near the outer surface of Ge film.

From the measured ellipsometric parameters of the reflected light wave one can determine optical constants (refractive and absorption indices) of the film, as well as its thickness and the refractive index of an oxide layer on its surface. This is done using the iteration technique [17], provided that the number of unknown parameters does not exceed two. If, however, the ellipsometric data are obtained for the same structure at different (unknown) thickness of the surface oxide layer, then one can bypass the problem of iteration procedure divergence and determine all the four pa-

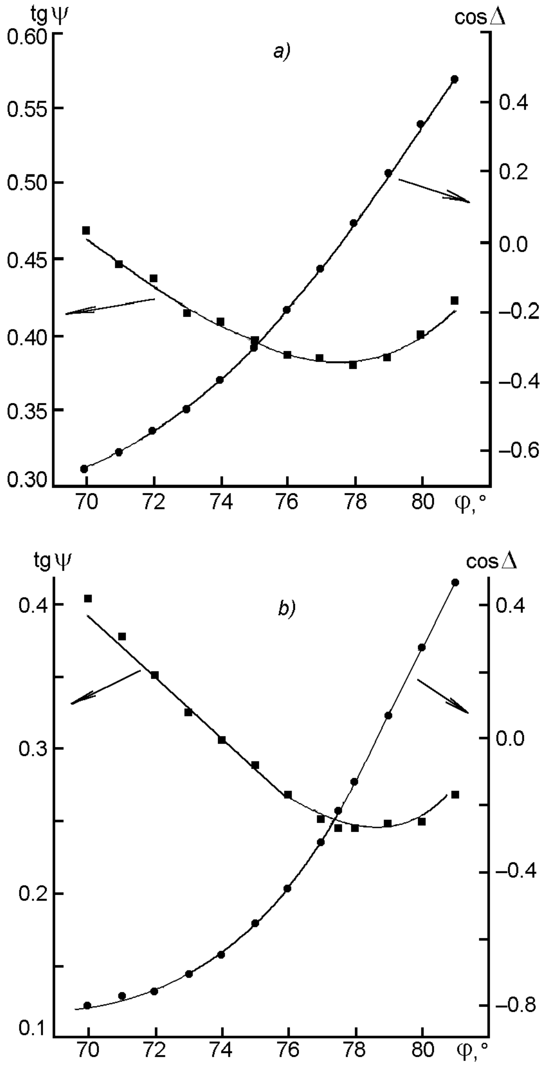

Fig. 2. Ellipsometric parameters vs angle of incidence curves at a wavelength a — $\lambda = 435$ nm and b — $\lambda = 579$ nm. The curves were calculated from the ellipsometry equation using the following parameter values: a — $n_3 = 4.723$, $k_3 = 2.642$, $n_1 = 2.14$, $d_1 = 5.2$ nm and b — $n_3 = 5.256$, $k_3 = 1.464$, $n_1 = 2.09$, $d_1 = 5.5$ nm. Squares and circles — experimental results.

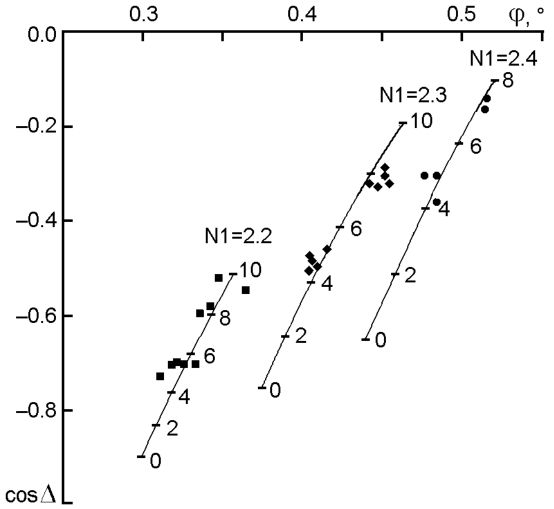

Fig. 3. Ellipsometric parameters of amorphous Ge films. The curves are calculated at different values of refractive index n_1 of the oxide layer. (*1* — 2.2, *2* — 2.3, *3* — 2.4). Squares and circles present the experimental results obtained at different degrees of oxide removal from the surface. The oxide layer thicknesses (in nm) are indicated at the curves.

rameters of a reflecting system, involving the unknown thicknesses of an oxide layer. Oxide layers formed on Ge surfaces are known to be not resistant against external factors [17]. That is why the used procedure of sample cleaning with a weak water solution of hydrogen peroxide for different time intervals (in the range of several minutes) provides different oxide layer thicknesses for the same surface of amorphous Ge. During the air exposure, the oxide layer thickness increased again. The refractive index of the oxide layer was assumed to be independent of the sample surface treatment.

From the measurements, a set of ellipsometric data was obtained corresponding to the same film (amorphous germanium) but to different oxide film thicknesses. The ellipsometric parameters, cos Δ and tg ψ, are different at each fixed angle of incidence. This makes it possible to determine the unknown parameters of a reflecting system. Fig. 3 illustrates the experimental data obtained for several wavelengths from the spectral range studied. The points in the figure correspond to the measured values obtained at different degrees of surface cleanness. The experimental pairs of cos Δ and tg ψ values fit in certain curves resembling theoretical ones describing the ellipsometric parameters in the case when only the oxide layer thickness is changed. We shall refer to these curves as the constant refractive index (CRI) curves. The CRI curves begin at a point corresponding to zero thickness of the oxide layer (i.e., to the case of amorphous Ge film free from oxide). In determination of both oxide layer and film parameters, the problem is how to find such the starting point position where the refractive index value for the oxide layer remains the same along the experimental CRI curve.

Table. Refractive index n_1 and thickness d_1 of the oxide layer, refractive index n_3 and absorption index k_3 of amorphous Ge at various wavelengths λ

λ, nm	n_1	d_1, nm	n_3	k_3	n_3 [12]	k_3 [12]
579	2.2		5.26	1.46	4.1	2.15
579*	2.09±0.03	5.5±0.1	5.26	1.46		
546	2.2	4	5.11	1.86		
492	2.4	4.2	4.96	2.30	3.5	2.6
435	2.3		4.72	2.64		
435*	2.15±0.02	5.2±0.2	4.72	2.64		
405	2.4	4.9	4.45	2.98	3	2.8
365	2.4	4.6	4.13	3.31		
313	2.5	4.3	3.67	3.79	2	3

* Obtained from multiangle measurements

We have determined the parameters of the germanium film and oxide layer in several stages using a self-consistent procedure. First, the distribution of experimental points in Fig. 3 was described using a square-law approximation formula. Then, the trial-and-error method was used to determine the starting point (i.e., cos Δ_0 and tg ψ_0) at the extention of the approximating curve providing the same value of the oxide layer refractive index at different points of the approximating curve. In this case, care was taken that thickness values corresponding to different wavelengths were the same. The oxide layer parameters were calculated using the iteration technique [17].

We managed to determine the required starting points for all the wavelengths studied. The corresponding theoretical curves that describe the obtained experimental data were calculated using ellipsometry equations for a single-layer system. These curves are shown in Fig. 3 with solid lines. The optical constants, n_3 and k_3, of the germanium film were calculated from the cos Δ_0 and tg ψ_0 values using the metal optics expressions [19] for a semi-infinite medium. The optical constants of the germanium film and parameters of the oxide layer on the film surface calculated for different wavelengths are given in Table. A great scatter in experimental values with respect to the oxidation curve is due to uncontrollable factors that accompany the etching process. Besides, different CRI curves are close to each other at small layer thicknesses (i.e., near the starting point). As a result, the refractive index is determined at a considerable error. The results obtained indicate that at small (below 10 nm) thicknesses the oxide layers studied were uniform. In fact, the experimental points for the samples of different degrees of surface cleanness fit in the CRI curves calculated within the single-layer model. Besides, the angular dependences of ellipsometric parameters calculated using the obtained values of optical constants agree well with the experimental results obtained from multiangular measurements (see Fig. 2).

The authors of [20] also observed that the structure of GeO_2 films (prepared using high-temperature oxidation of single-crystalline germanium) appeared uniform at thicknesses below 150 nm. A deviation from uniformity was observed at somewhat larger thickness values. Non-uniform GeO_2 films (obtained using stepwise high-temperature overgrowing) were also observed in [21]. The refractive index of the oxide layer obtained by us that drops from 2.5 to 2.1 in the 313–579 nm spectral range agrees with the value 1.9±10 % that was obtained in [22] at the 546 nm wavelength when oxidizing germanium at room temperature.

The authors of [20, 23] who studied films obtained by thermal oxidation of germanium at high temperatures relate these films to germanium dioxide, the refractive index being close to 1.65 at 632.8 nm. Ge oxidation in air results in formation of monoxide with its further fast oxidation to GeO_2 or, at least, decomposition into Ge and GeO_2 [17]. Therefore, there is a reason to believe that the oxide layers studied by us consist of Ge dioxide. Somewhat enlarged (as compared to the reference data) refractive index may be due to the existence of unbound Ge in the oxide layer bulk. The oxide layer thickness depends on the duration of film keeping in air and degree of surface cleanness. It is seen from Fig. 3 that for the samples studied the initial oxide layer thickness is about 8 nm. It may be reduced at least by half using etching in hydrogen peroxide.

In [12], ellipsometry was used to study germanium transition from amorphous to crystalline state in films deposited onto a substrate at different substrate temperatures. The measurements were performed on freshly prepared films, the optical constants were calculated without taking into account the oxide layer. The optical constant values obtained in [12] for the films prepared rather similarly to our case (at a substrate temperature of 100°C) are in good agreement with our results if our data were processed within the semi-infinite medium model (i.e., without accounting for oxide layer). Taking into account an oxide layer enabled us to obtain more reliable values for optical constants of amorphous Ge, differing considerably from the reference data (see Table). Thus, even on freshly prepared Ge films, there exists several nm thick oxide layer. It is to be taken into account when determining the optical constants of films (e.g., in the way used in this work). It should be noted that investigations of Ge optical constants in the visible spectral region are of great importance, since the spectral structure due to intraband transitions in the case of single-crystalline germanium is observed here. This structure is rather sensitive to the crystal state. It varies considerably depending on the Ge film preparation conditions. We have shown that it is also sensitive to the oxide layer thickness. That is why taking oxide layer into account is essential.

Thus, our ellipsometric studies enabled us to determine optical constants of both the amorphous Ge film and oxide layer on its surface. Considering the results obtained, the single-layer model has been shown to be suitable for multiangular ellipsometric measurements when light is reflected from amorphous germanium. This evidences that the oxide layer formed on the film surface in air is uniform. The oxide layer thickness after long-term keeping in air may reach 8 nm, its refractive index being close to that of germanium dioxide. Etching in aqueous solution of hydrogen peroxide reduces the layer thickness several times.

Spectral dependences of amorphous Ge optical constants have been obtained under account for oxide layer. These dependences evidence that there is no structure similar to that in the corresponding spectra of single-crystalline Ge. Taking an oxide layer on the Ge film surface into account enabled us to obtain more reliable values of optical constants for amorphous Ge.

References

1. Zh.I.Alferov, N.S.Zimogorova, A.M.Samol'yanov, M.K.Trukhan, *Ukr.Fiz.Zh.*, **9**, 659 (1964).
2. J.P.Donelly, A.G.Milnes, *Int.J.Electron.*, **20**, 295 (1966).
3. N.Chand, J.Klem, H.Morkoc, *Appl.Phys.Lett.*, **48**, 484 (1986).
4. T.V.Belousova, I.G.Neizvestnyi, Yu.G.Sadof'ev et al., *Fiz.Tekhn.Poluprov.*, **23**, 1955 (1989).
5. J.C.Marinace, *IBM J.*, **280** (July 1960).
6. V.M.Vald-Perlov, V.V.Veits, N.G.Ivashchenko, *Elektronnaya Tekhn., Ser.2. Poluprovodnikovye Pribory*, No.3, 15 (1983).
7. V.F.Mitin, Yu.A.Tkhorik, E.F.Venger, *Microelectronics J.*, **28**, 617 (1997).
8. V.F.Mitin, *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **2**, 115 (1999).
9. N.F.Mott, E.A.Davis, Electronic Processes in Non-Crystalline Materials, 2nd ed., Clarendon Press, Oxford (1979).
10. D.Beaglehole, M.Zavetova, *J.Non-Cryst.Solids*, **4**, 272 (1970).
11. T.M.Donovan, W.E.Spicer, J.M.Bennet, E.J.Ashley, *Phys.Rev.B.*, **2**, 397 (1970).
12. G.Jungk, *Phys.Stat.Sol.(b)*, **44**, 239 (1971).
13. J.Stuke, *J.Non-Cryst.Solids*, **4**, 1 (1970).
14. R.S.Bauer, *Sol.St.Commun.*, **10**, 1171 (1972).
15. T.M.Donovan, *J.Opt.Soc.Amer.*, **53**, 1403 (1963).
16. V.A.Odarich, *Zav.Lab.*, **43**, 1093 (1977).
17. A.E.Vol, Structure and Properties of Binary Metal Systems, Vol.2, Fizmatgiz (1962) [in Russian].
18. V.A.Odarich, V.I.Panasyuk, V.S.Staschuk, *Zh. Prikl.Spektrosk.*, **56**, 827 (1992).
19. Principless of Ellipsometry, ed. by A.V.Rzhanov, Nauka, Novosibirsk (1979) [in Russian].
20. V.N.Drozdov, T.I.Kovalevskaya, A.V.Rzhanov, K.K.Svitashev, *Mikroelektronika*, **2**, 46 (1973).
21. L.L.Vasil'eva, K.K.Svitashev, A.I.Semenenko et al., *Optika i Spektrosk.*, **37**, 574 (1974).
22. R.J.Archer, *Phys.Rev.*, **110**, 354 (1958).
23. E.B.Gorokhov, V.V.Grishchenko, in: Ellipsometry: Theory, Techniques, Applications, Nauka, Novosibirsk (1987) [in Russian].

Еліпсометричні дослідження плівок аморфного германію на підкладках із монокристалічного арсеніду галію

В.А.Одарич, О.В.Руденко, М.П.Семенько, Р.В.Конакова, В.Ф.Мітін, В.В.Холевчук

Проведено багатокутові еліпсометричні дослідження аморфних плівок германію, отриманих методом осадження у вакуумі на підкладки з напівізолюючого монокристалічного GaAs (100). Викладено методику обробки багатокутових еліпсометричних вимірів, котра дозволяє знайти параметри відбиваючої системи. Виявлено, що на поверхні плівок утворюється окисний шар від 4 до 8 нм завтовшки. Виміряно показники заломлення цього шару в спектральній області 313–579 нм і оптичні сталі плівки аморфного германію.