Eur. Phys. J. D **9**, 619–621 (1999)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

Size reduction-induced changes in the electron and phonon spectra of Ge nanostructures in the early stages of growth

P. Tognini[1], A. Stella[1], P. Cheyssac[2], R. Kofman[2], and C.E. Bottani[3]

[1] INFM - Dipartimento di Fisica "A. Volta", Università di Pavia, via Bassi 6, I-27100 Pavia, Italy
[2] Laboratoire de Physique de la Matière Condensée, UMR 6622, Université de Nice-Sophia Antipolis, F-06108 Nice Cedex 2, France
[3] INFM - Dipartimento di Ingegneria Nucleare, Politecnico di Milano, via Ponzio 34/3, I-20133 Milano, Italy

Received: 1 September 1998 / Received in final form: 10 November 1998

Abstract. An optical study of the early stages of growth of Ge nanoparticles embedded in amorphous alumina matrix is presented here. The growth technique is based on a surface tension-driven aggregation process, which presents some similarities with the stress-driven heteroepitaxy technique. The experimental findings (from near UV to far IR, i.e., from electronic to phononic structures) can be interpreted in terms of the presence of a wetting layer together with the nanoparticles when the deposited Ge quantity is below a given value. This layer disappears when the Ge quantity is sufficiently high and the coalescence aggregation becomes the dominant process.

PACS. 78.66.-w Optical properties of specific thin films, surfaces, and low-dimensional structures: superlattices, quantum well structures, multilayers, and microparticles – 81.10.Bk Growth from vapor – 68.65.+g Low dimensional structures (superlattices, quantum well structures, multilayers): structure and nanoelectronic properties – 78.30.-j Infrared and Raman spectra

An investigation of the optical properties of Ge nanostructures, grown by what was defined as an evaporation–condensation Volmer–Weber technique [1] and embedded in an alumina matrix, is reported here. In this paper, we concentrate our attention on the early stages of growth, in order to see if the surface tension-driven coalescence process, which leads to the formation of nanoparticles, depends on the quantity of deposited material. A wide spectral range, from about $100\,\mu$m to about $0.2\,\mu$m, i.e., from far infrared to near ultraviolet, has been covered for this reason, in order to obtain information on both the phonon and electron responses under size reduction, since the combined picture of electron and phonon behavior represents a fine tool for studying the modification of the physical properties of the nanoparticles under space confinement [2].

During the growth process, Ge vapor is deposited on an amorphous substrate; its partially nonwetting character is the driving mechanism for the formation of nanoparticles instead of a continuous layer; this formation occurs when the substrate temperature is kept sufficiently high to maintain the deposited material in the liquid state (for simplicity, in the following, we will refer to the deposited material quantity in terms of equivalent thickness, i.e., the thickness it would have if it were a layer instead of an ensemble of nanoparticles). This growth technique has been extensively described in [1, 3] for the case of metal (Sn) and semiconducting (Ge) nanoparticles, for a thickness of the deposited layer from about 13 to some hundred Å. It has also been pointed out that by alternating the deposition of Ge and Al_2O_3, one obtains a nearly three-dimensional uniform dispersion of nanocrystals in the amorphous matrix; nanoparticles have a truncated spherical shape (determined by the wetting angle, which is a consequence of the balance of the surface tensions during the deposition–coalescence process) and a Gaussian-like size distribution, with $\sigma/\mathrm{R} \leq 20\%$.

It has been assumed in a previous work [4] that when the Ge quantity is very low (under 13–15 Å), the constituent nanoparticles sit on a wetting layer (as in the Stransky–Krastanov process), while the full Volmer–Weber growth takes place only above this critical deposited value. In the case of Ge, the contact angle $\mathrm{Ge}-\mathrm{Al_2O_3}$ is $\approx 106°$ (i.e., considerably lower than the contact angle of the interfaces $\mathrm{Sn}-\mathrm{Al_2O_3}$ and $\mathrm{Pb}-\mathrm{Al_2O_3}$), so that the formation of the film is expected to be favored. Such a thin wetting layer, which is not directly observable, for instance, by transmission electron microscopy (TEM), bears a remarkable resemblance with the formation of quantum dots by means of the stress-driven heteroepitaxy, where reference is made to a wetting layer that is present only if the amount of deposited material does not exceed a critical value of a few lattice constants [5]. Here we present new data obtained by different techniques that consistently support the existence of such a layer also in the growth process above illustrated.

The samples investigated are grown by an alternate deposition of alumina and Ge on a hot sapphire substrate.

Table 1. Structural characteristics of the samples investigated by visible near-UV transmission and Raman spectroscopy. The nanoparticles average radius has been determined by TEM analysis. A wetting layer would be too thin to be detectable by this technique.

Sample	Number of alternate Ge depositions	Equivalent thickness (see text) (Å)	Nanoparticles nominal average radius (Å)
Ge6.6	12	6.6	9
Ge8	10	8	8
Ge10	8	10	19
Ge13.3	6	13.3	23
Ge16	5	16	32

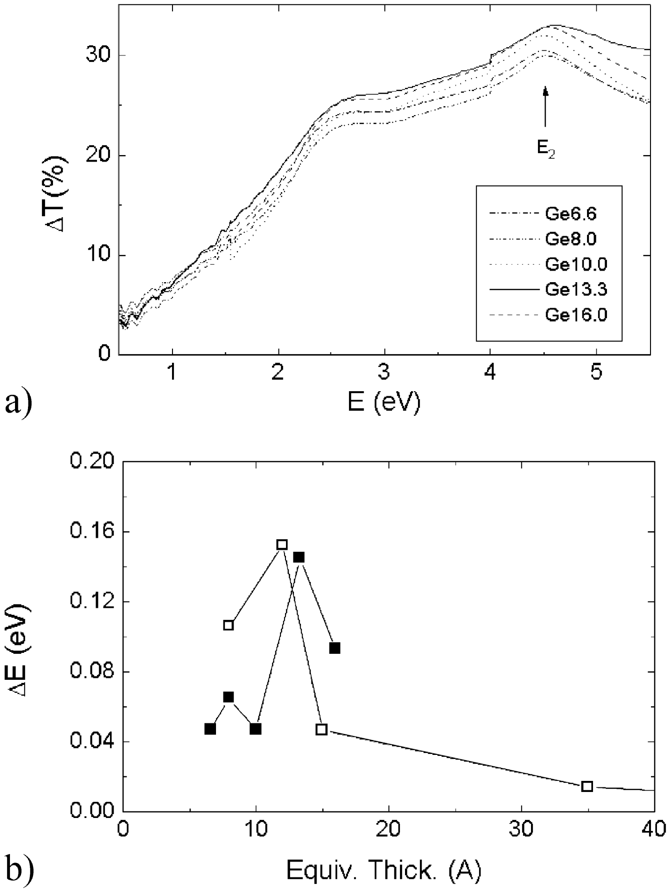

Fig. 1. (a) Transmittance difference ΔT (see text) spectra. (b) Shift of the peak corresponding to the structure E_2 with respect to the bulk versus the deposited Ge quantity. □ are data points concerning a previous series of samples, distributed on a wider range.

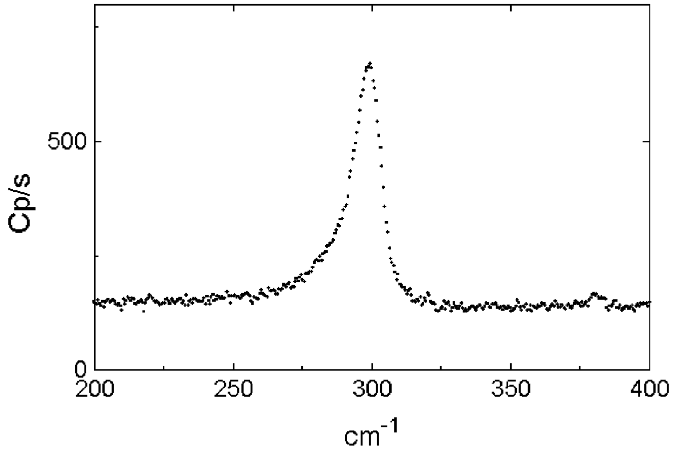

Fig. 2. Raman spectrum of the sample Ge10 in the spectral region of the crystalline Ge TO peak.

Their characteristics are summarized in Table 1. Optical spectra in the energy range from about 0.5 to about 5.5 eV have been collected using the spectrophotometer Varian Cary 5, with a spectral resolution of about 0.01 eV. The difference between the transmittance of a reference sample without Ge and the samples investigated (ΔT) is shown in Fig. 1a. A comparison with the bulk [6] confirms the good crystalline quality of the nanostructures. In Fig. 1b, the shift of the E_2 absorption peak with respect to the bulk position is reported; this structure originates in the Brillouin zone around the X point, the main contribution coming from a portion near the Chadi–Cohen special point $(3/4, 1/4, 1/4)$ [6]. It is possible to see that below an equivalent thickness of about 15 Å, there is a reduction of the blueshift, i.e., a reduction of the quantum confinement effect typical of quantum dots and previously observed in the size range between ~ 30 and ~ 130 Å on Ge nanoparticles [3].

In principle, one cannot exclude that in the case of complete nucleation, when the size is very small, the crystalline structure of Ge changes, and this affects the position of the electronic absorption peaks. In this respect, the crystalline structure of Ge present in the samples has been investigated.

In Fig. 2, the Raman spectrum of the sample Ge10 is shown. It would contain only cGe nanocrystals of 19 Å nominal average radius in the case of complete Volmer–Weber aggregation. Because of phonon confinement [2], the Raman peak is expected to be considerably below 300 cm^{-1}, which is the frequency of the transversal optical (TO) Raman active optic phonon of a perfect bulk Ge crystal; furthermore, the peak line shape should show a much stronger asymmetry. The maximum here is located instead at about 298 cm^{-1}, and only a small shoulder around 280 cm^{-1} gives evidence of confinement effects. This behavior can be attributed to the presence of a crystalline Ge film whose Raman spectrum is only slightly different

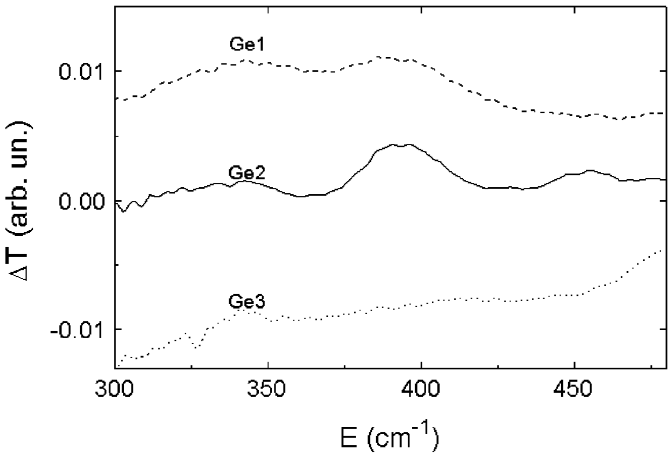

Fig. 3. Far infrared transmittance difference ΔT (see text) spectra of the samples Ge1 and Ge2. The main absorption structure (absent in the spectra of the matrix, as shown by the curve Ge3) is indicated. Ge1 and Ge2 are multilayered grown samples. Each Ge deposition on the sample Ge1 has an equivalent thickness of 15 Å, whereas the Ge layers in the sample Ge2 have a thickness of 8 Å.

from that of bulk Ge. It is worth noting that before full coalescence, because of the presence of the wetting layer, the confinement effect tends to disappear onto the plane of the sample.

In addition, far infrared transmission measurements have been performed using a Bruker Fourier–transform spectrophotometer, in the energy range between 300 and 450 cm^{-1}, on multilayer samples. For these measurements, the films have been evaporated on an Si substrate. Here we compare the optical response of a sample, which should contain Ge nanoparticles (Ge1) if the deposited quantity were above the critical value (condensation in the liquid phase), with the response of a sample containing continuous films obtained by evaporating Ge on a cold substrate (Ge2), preventing in this way the diffusion–coalescence effect. In Fig. 3, the transmission differences between a bare substrate and the two above described samples, respectively, are compared with a sample without Ge (Ge3). The relevant absorption peak at about 390 cm^{-1} in the spectra of sample Ge1 and Ge2 (which is absent in the spectrum of sample Ge3) is clearly due to Ge, although it is not present in the transmission spectrum of a bulk crystalline Ge [7]. It could be due to a surface mode, since such spectral features in nanostructures are often dominant [8], and they are sometimes expected at higher energy than the bulk transversal and longitudinal modes. The observation that the samples Ge1 and Ge2 have similar spectra may bring additional support to the presence of a Ge layer in the sample Ge1, also.

In conclusion, the optical properties of Ge nanostructures from far infrared to near ultraviolet have been investigated and discussed in the case of small deposited material quantity. The presence of a thin wetting layer is supported by the combined observations of a progressive reduction of the blueshift of the absorption structures because of the interband electronic transitions and the reduction of the redshift of the Raman line, and also by the additional evidence extracted from far infrared data. We have shown here that there are convergent indications supporting the existence of a wetting layer in the early stages of growth of Ge nanocrystals in the surface tension-driven coalescence process, also.

References

1. E. Sondergard, R. Kofman, P. Cheyssac, A. Stella: Surf. Sci. **364**, 467 (1996)
2. C.E. Bottani, C. Mantini, P. Milani, M. Manfredini, A. Stella, P. Tognini, P. Cheyssac, R. Kofman: Appl. Phys. Lett. **69**, 2409 (1996)
3. P. Tognini, L.C. Andreani, M. Geddo, A. Stella, P. Cheyssac, R. Kofman, A. Migliori: Phys. Rev. B **53**, 6992 (1996)
4. P. Tognini, A. Stella, M. Geddo, P. Cheyssac, R. Kofman: 23th Int. Conf. Phys. Semicon. Processes **2**, 1633 (1996)
5. M. Grundmann, O. Stier, D. Bimberg: Phys. Rev. B **52**, 11 969 (1995)
6. M.L. Cohen, J.R. Chelikowsky: *Electronic Structure and Optical Properties of Semiconductors* (Springer, Berlin 1989)
7. J.R. Aronson, H.G. McLinden, P.J. Gielisse: Phys. Rev. **135**, A785 (1964)
8. R. Ruppin, R. Englman: Rep. Prog. Phys. **33**, 149 (1970)