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IR laser CVD of nanostructured Si/Ge alloy from silane–germane mixture

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ABSTRACT

IR laser irradiation of an equimolar silane–germane mixture in Ar results in the decomposition of both compounds and allows chemical vapour deposition (CVD) of solid nanostructured Si/Ge film that was analyzed by FTIR and Raman spectroscopy, X-ray diffraction and electron microscopy. The film is deduced to be formed via coalescence/intermixing of extruded Si and Ge atoms and revealed as metastable and consisting of the crystalline d-c Ge and crystalline Si/Ge alloys embedded in an amorphous Si and Si/Ge phase. The reported IR laser CVD of the nanostructured Si/Ge film represents a simple way for synthesis of binary alloys from volatile hydride precursors.

1. Introduction

There is a great recent interest in synthesis of Si_xGe_{1-x} alloys, which is due to their electronic properties and applications in optoelectronics and technologies for constructing integrating circuits (e.g. [1,2]). Silicon and germanium are miscible in all proportions and a number of structural varieties of their alloys have been prepared by several techniques. For example, crystalline SiGe alloys and strained SiGe layers have been obtained by molecular beam epitaxy [3,4] and UHV chemical vapour deposition (CVD) [5], fully amorphous alloys have been produced by plasma-enhanced CVD [6,7], polycrystalline films containing both crystalline and amorphous phase were fabricated by reduced pressure CVD [8], relaxed thin films were acquired by ion implantation technique [9], highly coherent SiGe and Si_4Ge nanostructures were synthesized by molecular beam epitaxy from single-source Si–Ge bonds-containing hydrides [10] and finally SiGe nanocrystallites in a-Si_xGe_{1-x}:H matrix [11] were deposited by a plasma CVD process or by sputtering of Si and Ge in hydrogen [12].

The CVD methods, belonging among the most studied approaches for growing SiGe films, make mostly use of silane and germane (or digermane) as Si and Ge precursors and a hot surface to induce heterogeneous decomposition (e.g. [13–16]).

The heterogeneous effect of hot surfaces in thermal (conventional) decompositions of the gaseous precursors is obviated by irradiating these compounds with UV or IR laser and inducing homogeneous decomposition of both precursors at low substrate temperature. Examples of these co-decompositions have been presented and they concern the UV laser co-photolysis of SiH_4–GeH_4 [17] or Si_2H_6–GeH_4 [18] for CVD of amorphous Si/Ge films and the TEA CO_2 laser co-decomposition of silane and germane for synthesis of $Si_{1-x}Ge_x$ nanocrystals [19].

We have recently used the TEA CO_2 laser for inducing (i) dielectric breakdown in tetramethylgermane/tetramethyltin mixtures to allow CVD of nanostructured Sn/Ge/C and Ge–Sn/C films [20] and (ii) infrared multiple-photon co-decomposition of two different metal hydrides (SnH_4, GeH_4 or SiH_4) for CVD of nanodisperse Ge–Sn [21] and β-Sn/SnSi [22] alloys. These nanosized alloys are expected to have photoluminescence properties controlled by their composition [19] and can find applications in biology and medicine.

Our next attention has been given to homogeneous IR laser-induced co-decomposition of silane and germane and we now report on structure of a solid Si/Ge product formed from these two precursors in the CVD process.

2. Experimental

IR-laser irradiation experiments were conducted in a Pyrex reactor (70 mL in volume) reported previously [21]. Briefly, the reactor was a tube fitted at each end with KBr windows and having a PTFE valve connecting to vacuum manifold and pressure transducer. The laser pulse was focused with a Ge lens (f. l. 15 cm) to the centre of the reactor, above which was accommodated a Cu or a NaCl substrate. The samples of silane and germane (each 5 Torr) in Ar (total pres-

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sure 110 Torr) were irradiated by a pulsed 1300 M TEA tunable CO_2 laser (Plovdiv University) that operated with a frequency of 1 Hz on the P(20) line of the $00^01–10^00$ transition (944.19 cm^{-1}), the full width at half maximum (FWHM) of 150 ns and a pulse energy of 1.8 J. Thin films were deposited at incident fluence of 7.2 J cm^{-2} with 45 pulses through 3 cycles.

The progress of the co-decomposition of silane and germane was monitored by FTIR spectroscopy (a Nicolet Impact spectrometer) using absorption bands at 908 and 2186 cm^{-1} (SiH_4) and 816 and 2108 cm^{-1} (GeH_4). After the irradiation, the reactor was evacuated and the Cu substrate was transferred in sealed vials under Ar for the measurements of its properties by different physical methods.

FTIR absorption spectra were measured on a Nicolet Impact spectrometer (120 scans, resolution 4 cm^{-1}) and Raman spectra (32 scans, resolution 2 cm^{-1}) were recorded using a dispersive Raman instrument Nicolet Almega XR with the excitation wavelength 473 nm and power 10 mW.

SEM analyses were carried out on a Philips XL30 CP scanning electron microscope and energy dispersive X-ray (EDX) analyses were conducted on a Philips XL30 CP instrument equipped with an EDX detector PV 9760 using accelerating voltage 5–30 kV.

TEM (transmission electron microscopy) and HRTEM (high-resolution transmission electron microscopy) micrographs were obtained with on a JEOL JEM 3010 microscope operated at 300 kV (LaB_6 cathode, point resolution 1.7 Å) with an attached EDX (energy dispersive X-ray) detector. A copper grid coated with a holey carbon film was used to prepare the samples. The Si/Ge film was scratched and transferred onto a grid and used for the TEM observation.

Diffraction patterns were collected with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Co K_α radiation, 40 kV, 30 mA, point focus), an X-ray monocapillary with the exit diameter of 0.1 mm, and a multichannel detector X'Celerator with an anti-scatter shield. A sample holder for single crystal XRD measurement was adopted by adding *z*-(vertical) axis adjustment (Huber 1005 goniometer head). The angle of the incident beam (omega) was fixed to 2° to suppress the penetration depth and enhance the signal of the deposited thin layer. XRD patterns were recorded as reported previously [21].

Qualitative analysis was performed with the HighScore software package (PANalytical, The Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database [34]. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (Bruker AXS, Germany, version 4.1) with structural models based on ICSD database [23]. This program permits to determine the unit cell parameters and to estimate the weight fractions of crystalline phases and also to estimate the amorphous content (the "degree of crystallinity") by means of Rietveld refinement procedure.

Silane (Lachema, >99.9% pure) and germane (>99% pure, obtained by reaction of germanium dioxide with potassium tetrahydroborate [24]) were distilled on vacuum line and checked for purity prior to use by FTIR spectroscopy.

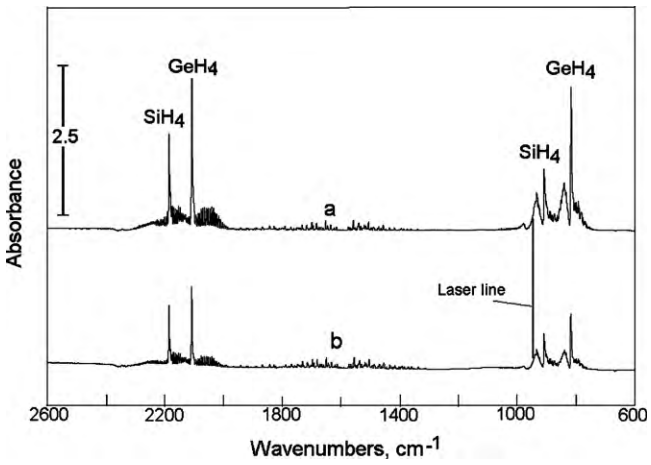

Fig. 1. FTIR spectrum of GeH_4 and SiH_4 mixture (each 5 Torr) in Ar (total pressure 100 Torr) after 45 pulses irradiation with unfocused (a) and focused (b) laser pulse.

3. Results and discussion

The unfocused TEA CO_2 laser irradiation of gaseous SiH_4 (5 Torr)–GeH_4 (5 Torr)/Ar (100 Torr) mixture with the laser tuned to the absorption band of silane (R-branch transition of the ν_4 mode [25], Fig. 1a) results in no decomposition. Nevertheless, with the focused radiation, we observed a visible spark and silane and germane decomposing at a similar rate (respectively depleting by 35 and 45% with 45 pulses) and allowing deposition of an ultrafine solid on the Cu substrate. The observed depletion of absorption bands of the Si and Ge hydrides (Fig. 1b) is indicative of infrared multiple-photon decomposition (IRMPD) of SiH_4 [25–27] and a collisionally-assisted decomposition of non-absorbing germane [28,29]. We admit, however, that the visible spark, the high pressure of Ar and the higher depletion of germane than that of silane can be also consistent with more feasible homolytic fission of the Ge–H bond and with some contribution of charged species produced in dielectric breakdown [30,31].

SEM images of the solid deposit (Fig. 2) show fluffy morphology with sub-μm-sized bodies that associate into several μm large agglomerates. The EDX analysis indicates low contamination by O and C elements and reveals average stoichiometry $Ge_{1.00}Si_{0.64}C_{0.05}O_{0.06}$. This value corresponds to the relative depletion of silane and germane and it is compatible with a complete use of Si and Ge elements for the formation of solid deposit.

FTIR spectra of the deposit (Fig. 3) do not exert characteristic absorption bands of Si–H and Ge–H bonds located at 1900–2250 cm^{-1} and are in agreement with virtual absence of Si_xGe_{1-x}:H structures [32,33]. However, the spectra reveal [34] very weak absorptions at 2260 and 2200 cm^{-1} together with a strong ν(SiOSi) band at 1070 cm^{-1}, a weak ν(GeOGe) band at 880 cm^{-1} and δ(SiOSi) and δ(H_nSiO) shoulders at 840 and 985 cm^{-1}, all of which

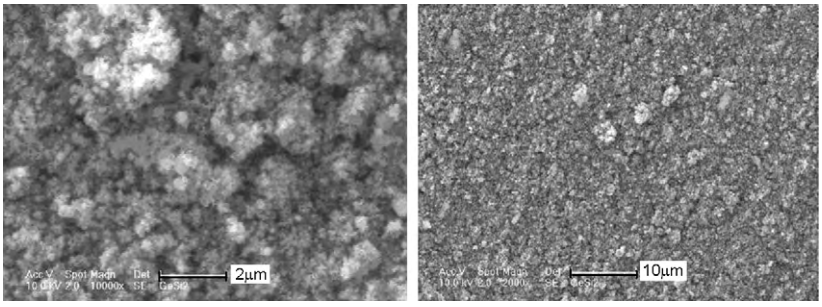

Fig. 2. Typical SEM images of the deposit.