Growth of Ge nanowires by chemical vapour deposition technique

A.R. Phani*, V. Grossi, M.Passacantando, L. Ottaviano and S. Santucci
CASTI, CNR-INFM Regional Laboratory, Department of Physics, University of L'Aquila
Via Vetoio 10 Coppito 67010 L'Aquila ITALY

ABSTRACT

Germanium, have been synthesized using chemical vapor deposition with Au nanoparticles (with size ranging from 5 nm to 30 nm) as nucleating centers (catalysts) and Germanium powders as a source for the nanowires growth. Au nanoparticles were synthesized on Si (100) by using simple and cost effective sol-gel process from $HAuCl_4$ as a precursor. The monodisperse, molecular-scale, single-crystal Ge nanowires with diameters as small as 15 nm have been grown in a controllable manner. X-ray diffraction and high resolution scanning electron microscopy and X-ray photoelectron spectroscopy have been employed to characterize for their structural, morphological, and compositional properties. These nanowires are opening up unique opportunities for fundamental physics and high-performance devices also the nanowires could be used to create electronic devices for small, ultra fast computers and memories.

Keywords: *Sol-gel process, Au nanoparticles, Ge nanowires, Chemical vapor deposition, X-ray diffraction*

I. INTRODUCTION

A wide field for novel electronic applications opens at the bottom of the length scale accessible by modern semiconductor deposition techniques. Among these semiconductor materials, Germanium nanowires (GeNWs) is an excellent electronic material with renewed interest for future computing and has attracted lot of attention in recent years [1-3] owing to the advanced electrical properties of Ge as high carrier mobilities [4]. Various deposition methods for crystalline GeNWs have been reported using Au nanoparticles as nucleating seeds, including chemical vapor deposition [5], physical vapor deposition [2-3], solvothermal reactions [6].

On the other hand, a variety of metallic nanostructures, including particles, prisms, plates, rods, and wires, have generated significant scientific and technological interest because of their unique optical properties as well as their novel chemical and catalytical properties for the growth of semiconductor nanowires. Among them, gold nanostructures with well defined dimensions represent a particular class of interesting nanomaterials to synthesize and study because of their wide practical applications. In fact, gold nanoparticles have recently been synthesized under microwave heating (480-1110W) by reducing $HAuCl_4$ in the presence of methanol, N,N-dimethylformamide by several investigators [7-9]. More recently, polygonal gold nanoplates have been synthesized by the reduction of $HAuCl_4.4H_2O$ in ethylene glycol in the presence of Polyvinyl Pyrolidone (PVP) under microwave heating [10]. In the present investigation, microwave dielectric heating of the spin coated sol-gel solution containing Au nanoparticles, which is a promising technique for the growth of size controlled metallic nanostructures due its rapid heating and penetration has been applied.

II. EXPERIMENTAL PROCEDURE

In the present investigation, gold nanoparticles were obtained by reduction of $HAuCl_4$ sol-gel solution in the presence of ethylene glycol and polyvinyl alcohol. The details of the preparation of the gold nanoparticles under different conditions including a comparison of conventional annealing process and microwave irradiation have been reported elsewhere [11].

In brief, calculated quantity of $HAuCl_4.4H_2O$ has been weighed and dissolved in 15 ml 2-methoxy ethanol solvent and stirred for 30 min. To the above contents calculated quantity of ethylene glycol and polyvinyl alcohol have been added drop wise and stirred for 1 h. The obtained stock solution is used for dip coating purpose. The purpose of adding ethylene glycol is to reduce the Au^{+3} to Au° as shown in the following reactions:

$$CH_2OH\text{-}CH_2OH \longrightarrow CH_3CHO + H_2O$$

$$2CH_3CHO + HAu^{+3}Cl_4 \longrightarrow Au° + 4HCl + 3CH_3COCOCH_3$$

The formed nanoparticles were well dispersed because of the presence of polymeric surfactant PVA that could chemically adsorb onto the surface of gold solid. Sol-gel ultra thin films based on this solution have been prepared by a dip coating (rate: 4cm/sec) technique on to Si (100) substrates. The as deposited (xerogel) ultra thin films were then exposed to microwave 900W power for 10 min, resulting nanoparticles of Au with size ranging from 20- 40 nm in diameter.

The Au nanoparticles deposited on Si substrate and exposed to 900W microwave power for 10 min have been placed in the CVD chamber as shown in the figure 1.

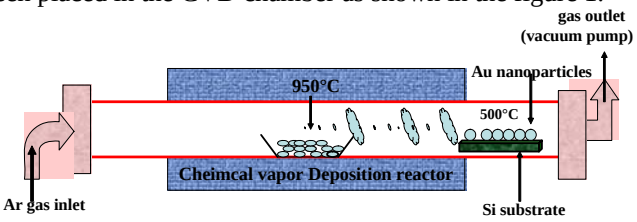

Figure1: Schematic diagram of the CVD reactor to grow Ge nanowires using Au nanoparticles as nucleating seeds

The deposited and exposed Au nanoparticles deposited on Si were placed in the CVD reactor 21cm (on right side, which has been optimized distance for the growth of GeNWs) away from the center of the reactor. Pure Ge powder was placed in an alumina crucible and placed at the center of the reactor as shown in the Figure 1. The system was pumped down to 10^{-6} Torr and later the reactor was slowly heated up to the desired temperature (950°C) in order to evaporate the Ge powder under the flux of pure Ar gas. During the evaporation the system was maintained at 5 Torr pressure. The total duration of the deposition was 30 min and the substrates were cooled in side the reactor till they reached room temperature. The deposited Ge nanowires were then removed from the reactor and then immediately placed in a vacuum decicator prior to the characterization.

The phase analysis, microstructure, and elemental composition of the gold nanoparticles exposed to microwave power (section 4) as well as Ge nanowires grown on Au nanoparticles (section 5) were characterized by employing high resolution scanning electron microscopy (HRSEM), X-ray photoelectron spectroscopy (XPS) analysis, X-ray diffraction (XRD) techniques, respectively.

III. RESULTS AND DISCUSSIONS

4. Characterization of Au nanoparticles

4.1. XRD

To evaluate the phase formation of the formed nanoparticles of Au, Glancing Incidence X-Ray Diffraction (GIXRD) (model Bruker D5000) technique has been employed with θ fixed at 0.5°. The X-ray source was a sealed X-ray 1.5 kW Cu radiation (λ=1.5406 Å). XRD pattern obtained for the pure Au nanoparticles exposed to 900W microwave power for 10 min has been shown in the figure 2. The measured reflections were very high intensity with narrow peaks indicating high crystallinity, whose grain size has been calculated using the well known Scherrer equation applied to (111) plane (which is the maximum reflection of the cubic phase of Au) and were found to in the order of 22 ± 3 nm.

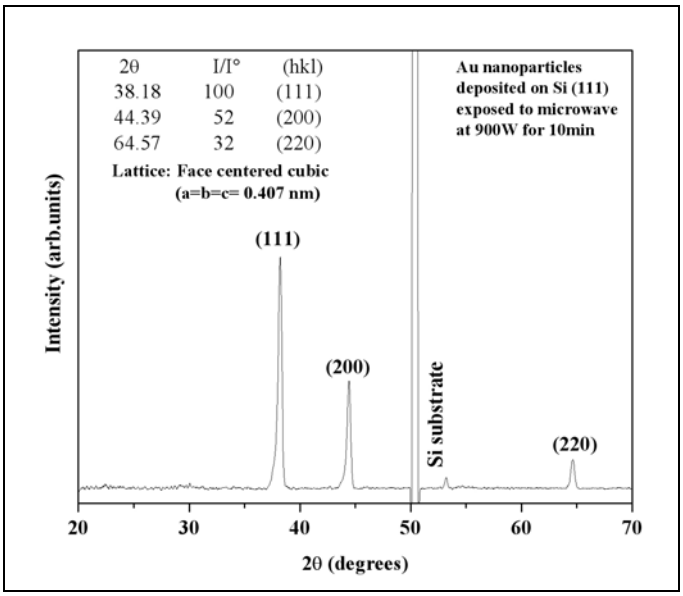

Figure 2: XRD pattern of gold nanoparticles deposited on Si substrate and exposed to 900W microwave power for 10 min.

All the diffraction planes belonging to cubic phase of Au agree very well with reported values and match with JCPDS data (card #: 04-0784) confirming the formation of face centered cubic phase. From the spectra the lattice parameters (a = b = c = 0.407 nm) have been calculated and found to be in good agreement with the JCPDS data.

4.2. SEM

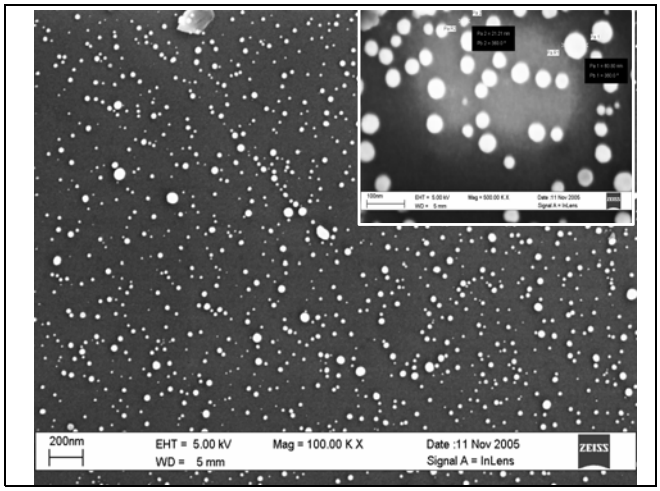

Figure 3: SEM images (high magnification image in the inset) of gold nanoparticles on Si substrate exposed after irradiation with microwave 900W power for 10 min.

Morphological studies on the irradiated ultra thin films of Au have been carried out by employing high resolution scanning electron microscopy (model: ZIESS). Low magnification (large area) and high magnification images

(in set) of Au nanoparticles deposited on Si substrate and exposed to microwave power 900W for 10 min have been shown in the Figure 3. It is evident from the figure that the formed nanoparticles have varied size raging from as low as 5 nm to as big as 40 nm. The average size of the particles was found to be 25 nm.

5. Characterization of Ge nanowires

5.1. XRD

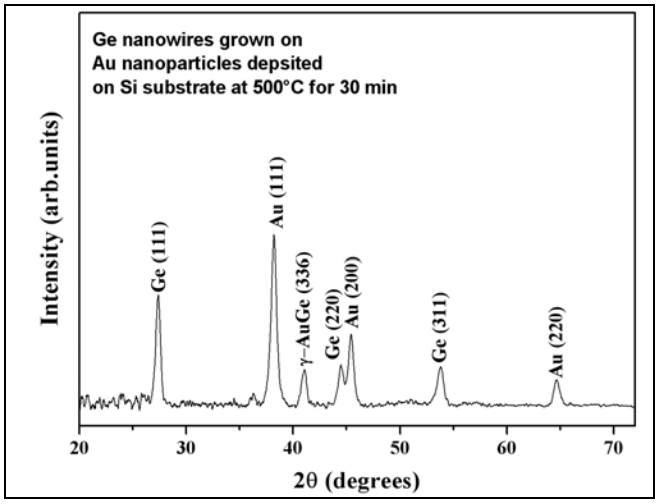

Figure 4: XRD pattern of Ge nanowires (grown Au nanoparticles) deposited on Si (100) substrates by using chemical vapor deposition using Ge powder as source for 30 min

XRD pattern Ge nanowires grown on Au nanoparticles previously grown on Si substrate at 500°C for 30 min has been shown in the Figure 4. The measured reflections belong to cubic phase of Ge apart from cubic phase of Au. All the diffraction planes belonging to cubic phase of Ge agree very well with reported values and match with JCPDS data (card #: 04-0545) confirming the formation of face centered cubic phase. From the spectra the lattice parameters (a = b = c = 0.45 nm) have been calculated and found to be in good agreement with the JCPDS data.

It is noteworthy to mention here that a new phase of γ-$Au_{0.6}Ge_{0.4}$ has appeared at 2θ = 40.75° (d = 0.221 nm). This alloy formation could obviously take place at the interface of Au nanoparticle and Ge nanowire. The observed 2θ, "d" and measured crystallite size for Au nanoparticles (using well know "Scherrer" equation), intensity, (hkl) planes and lattice parameters were tabulated in the table I.

Table I: Crystallite size, observed and literature values "d"(inter-planar distance, observed 2θ, lattice parameters

Phase	obes.2θ	d (nm)	D (nm)	I / I°	hkl	Lat.Par
Au (cubic)	38.15	0.235	22	100	111	a =
	44.39	0.204		52	200	b =
	64.57	0.144		32	220	c = 0.41
Ge (cubic)	27.28	0.326		100	111	a =
	45.30	0.20		57	220	b =
	53.69	0.17		39	311	c = 0.45
γ-$Au_{0.6}Ge_{0.4}$ (tetragonal)	40.75	0.221		100	336	

5.2. SEM

Figure 5 depicts the nanowire growth of Ge on to Au nanoparticles at substrate temperature of 500°C. The obtained nanowires were as small as 5 nm in diameter as

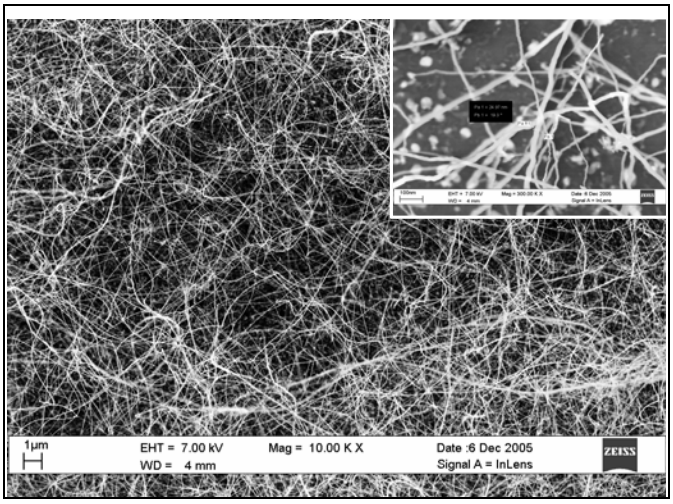

Figure 5: SEM images (high magnification image in the inset) of Ge nanowires (grown on gold nanoparticles) deposited on Si substrate by chemical vapor deposition technique for 30 min using Ge powder as source.

big as 30 nm. This varying size depends on the Au nanoparticles used as nucleating seed.

The inset of Figure 5 shows the high resolution SEM image of the Ge nanowires indicating the growth was took pace only on some Au nanoparticles. This behavior is yet to be investigated. We have obtained two kinds of Ge nanowires with different narrow distribution of 15 and 25 ± 1 nm. More detailed observation of the deposited Ge nanowires by high resolution transmission electron spectroscopy, Ge doped Mn and their electrical properties have been reported elsewhere [12].

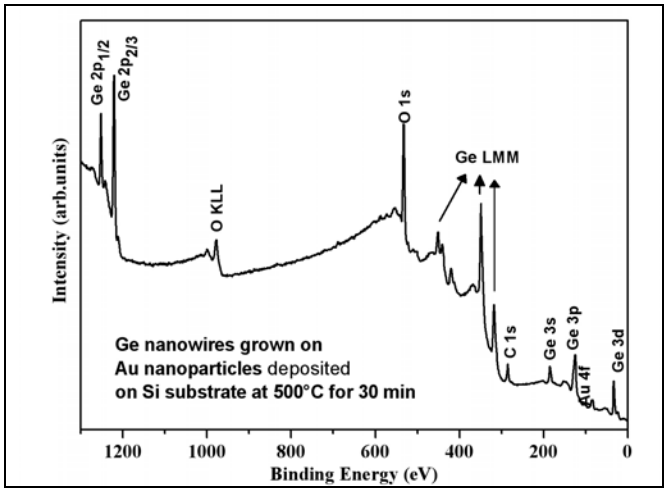

Figure 6: XPS survey of Ge nanowires grown on gold nanoparticles deposited on Si (100) by CVD process using Ge as source.

5.3. XPS

X-ray photoelectron spectroscopy (XPS) measurements of the Ge nanowires deposited on Au nanoparticles have been performed using the PHI ESCA system equipped with a Al X-ray source (hν =1253.6 eV) with a hemispherical analyzer. The XPS analysis of the Ge nanowires on Au nanoparticles have been surveyed in the binding energy (BE) range of 0-13000 eV, on 0.8 mm × 0.8 mm area as shown in the Figure 6. No contamination species were observed within the sensitivity of the instrument apart from the adsorbed atomospheric carbon. The binding energy (BE) calibration of the spectra has been

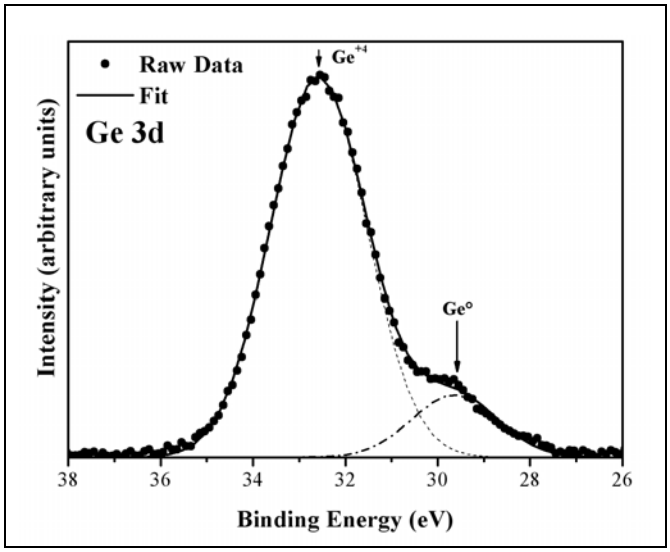

Figure 7: XPS core level spectra of Ge 3d

referred to carbon 1s peak located at BE = 284.54 eV. After convolution of the Ge3d core level spectrum, it is evident that there is slight formation of the GeO_2 on the surface of the formed ge nanowires. This oxide layer is as thin as 6 nm. The convoluted spectra of Ge 3d indicates the binding energy of Ge° at 29.4 eV and that of Ge_{+4} at 33.2 eV, respectively. This observation is very well coincided with the XPS database [13]. No alloy formation of γ-$Au_{0.6}Ge_{0.4}$ has been observed in XPS spectra, attributing this formation of alloy at the surface of gold particle, which later hindered by the grown Ge nanowires.

IV. CONCLUSIONS

Germanium, (Ge) nanowires have been synthesized using chemical vapor deposition with Au nanoparticles (with size ranging from 5 nm to 10 nm) as nucleating centers (catalysts). Au nanoparticles were synthesized on Si (100) by using simple and cost effective sol-gel process from $HAuCl_4$ as a precursor. The monodisperse, molecular-scale, single-crystal Ge nanowires with diameters as small as 15 nm have been grown in a controllable manner. X-ray diffraction indicates the growth of Ge in cubic phase with preferential orientation of (111). The deposited nanowires were as thin as 15 nm which could be applicable for electronic applications. The radical innovation in the present investigation is that we obtained narrow sized as low as 15 nm (covering the surface 45%) and 25 nm (covering the surface 55%) Ge nanowires using Au nanoparticles as nucleating seeds compared to results obtained so far in the literature.

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