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Deposition of Germanium Nanowires from Hexamethyldigermane: Influence of the Substrate Pretreatment

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Germanium nanowires (GeNWs) were synthesized by low pressure chemical vapor deposition of hexamethyldigermane  $(GeMe_3)_2$  at 490°C and a pressure of 90–100 Pa. GeNWs of several nanometers in diameter and a few micrometers in length were deposited onto substrates made of stainless steel, Fe, Mo, Ta, W, Si, and SiO<sub>2</sub>. The influence of surface pretreatment of the substrates (roughening of surface, grooves made by a diamond tip or Ge thermal evaporation) is discussed. GeNW deposits were studied using scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared, Raman spectroscopy, and energy-dispersive X-ray analyses. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3476288] All rights reserved.

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Nowadays, the progress in microelectronics has been driven by nanoscale technology for two- and one-dimensional structures. Therefore, nano-objects [nanowires (NWs), nanotubes, nanorods, nanopillars, nanoribbons, etc.] made of novel materials and alloys with unique properties have been studied and tested in detail in microelectronic systems. Gradually, such nano-objects are implemented into silicon technology to update and enhance the power and efficiency of microelectronic circuits, solar cell arrays, catalyst systems, etc.

Germanium is considered to replace silicon in some applications as it has a higher electron and hole mobility (3900 and 1900 cm<sup>2</sup>/V s, respectively) than silicon (1500 and 450 cm<sup>2</sup>/V s, respectively). Moreover, the Bohr radius of germanium is larger (24.3 vs 4.3 nm for silicon) and, therefore, quantum phenomena are more readily established.<sup>1</sup> Field emission transistors using germanium nanowires (GeNWs) have already been reported.<sup>2-4</sup>

The most commonly used methods for the preparation of GeNWs are the vapor–liquid–solid (VLS) technique and the seed-assisted deposition processes using catalyst nanoparticles (mostly Au).<sup>5-7</sup> However, the seeds act as traps for free charge carriers and therefore shorten their lifetime. The seed atoms could also migrate through the circuit structure and degrade its electronic properties. Although some attempts were made to manufacture NW microelectronic structures using Au seed nanocolloids,<sup>8,9</sup> the whole manufacturing process is complicated by the steps of introducing and removing Au nanoparticles from the fabricated NW structure.

A solution to this problem is based on a noncatalyst process that avoids using heteroatom seeds. Some of them seem not to be convenient for standard microelectronic arrays because they anticipate other chemicals as in electrochemical etching applying a HCl-containing aqueous electrolyte.<sup>10</sup> The best results of the noncatalyst growth of GeNWs have been obtained by chemical vapor deposition (CVD) procedures.

The first approach relates to the idea of intermetallic sites serving as initial centers of GeNW growth. Mathur et al.<sup>11</sup> proposed an intermetallic concept of the self-catalyst initial stage of GeNWs grown onto iron substrates. They assumed the formation of Fe–Ge intermetallic nuclei on an iron substrate during the initial steps of CVD performed at 325°C using a Ge(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> precursor. However, this approach is correct if germanium forms an alloy with the substrate material at the corresponding temperature.<sup>12</sup>

The second approach addresses a selection of a substrate and/or an appropriate surface modification before CVD deposition. Park et al. used a high porosity Si substrate<sup>13</sup> and Kim et al.<sup>14</sup> etched Si substrate with ultrapure water to form a highly reactive  $SiO_x$  superficial surface layer. Evidently, the structural and morphology surface conditions induce a generation of energetically favorable nucleation sites on a substrate for the consecutive GeNW growth.

Our motivation to prepare GeNWs using a noncatalyst-assisted low pressure chemical vapor deposition (LPCVD) procedure was (i)to avoid heteroatom seeds; (ii) to obtain GeNWs as thin as possible to ensure establishing of small confined quantum effects; and (iii) to explain the triggering mechanism of noncatalyst GeNW growth.

# Experimental

Sample preparation.— GeNWs were deposited by LPCVD of hexamethyldigermane (GeMe<sub>3</sub>)<sub>2</sub> (Aldrich, technical grade, 993-52-2) onto stainless steel, Fe, Mo, Ta, W, Si, and SiO<sub>2</sub> substrates. The reactor was evacuated by a Pfeiffer Vacuum TCP 380 turbopump to a base pressure of  $\sim 10^{-4}$  Pa. The CVD procedure proceeded in a furnace (Thermolyne 21100) for  $\sim 40$  min in the flow mode at 490°C and a pressure of 90–100 Pa.

Substrates and their pretreatment.— Various substrates with an area of  $1-2 \text{ cm}^2$  were tested for the growth of GeNWs: commonly used industrial steel, stainless steel (Goodfellow, AISI 310), tantalum (Aldrich, 99.9 + %), tungsten (Aldrich, 99.9 + %), molybdenum (Aldrich, 99.9 + %), iron (Aldrich, 99.9 + %), Si(100), and SiO<sub>2</sub>. The material of the substrate was selected with respect to the formation of the alloy with Ge at a corresponding temperature in the furnace (490°C). Gaudet et al.<sup>12</sup> studied thermally induced reactions of the germanium substrate with 20 transition metals and found that Fe forms an intermetallic alloy with Ge under 500°C, Mo and Ta above this temperature, and W does not form an alloy at all. Before the deposition, the substrates were cleaned in an ultrasonic bath in acetone (Aldrich). Both the untreated and pretreated substrates were used for the deposition.

Except the steel, all metal substrates were sequentially polished by a diamond paste with a mean diameter of grain ranging from 1 to 5  $\mu$ m. Subsequently, half of each substrate was roughened by a sandpaper [fine 800 diameter of grain (13  $\mu$ m), medium (360 – 30  $\mu$ m), and rough (80–200  $\mu$ m)]. The surface roughness (parameter  $R_a$ ) was determined by an instrument for the measurement of surface texture (Surtronic 3+, Taylor Hobson). The parameter  $R_a$ was 0.4  $\mu$ m for Mo, Ta, and W substrates and 0.6  $\mu$ m for the Fe substrate. A few grooves several millimeters long were scratched on Ta and Mo substrates by the diamond tip.

Silicon substrates were etched with 40% HF to remove a superficial thin  $SiO_x$  layer formed on the surface and subsequently rinsed by deionized water. To initiate the GeNW growth, Si and  $SiO_2$  substrates were modified by Ge thermal evaporation. The substrates

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were placed 1 cm from the downstream end of the furnace and exposed for 20 min to thermally evaporated Ge generated by heating a lump of Ge at 950-955 °C inside the furnace.

*Methods of characterization.*— Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses were done on a Philips XL30 CP instrument equipped with an EDX detector PV 9760. The accelerating voltage ranged from 5 to 25 kV, depending on the thickness of the deposited layer.

Transmission electron microscopy (TEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB<sub>6</sub> cathode, point resolution 1.7 Å). Images were recorded on a Gatan charge-coupled device camera with a resolution of  $1024 \times 1024$  pixels using the Digital Micrograph software package. Deposits were transferred onto a holey carbon-coated copper grid by brushing the grid dipped in ethanol against the substrate plate containing the deposit.

The Fourier transform infrared (FTIR) measurements of the deposits on tantalum substrates were performed on an FTIR spectrometer Nicolet Impact 400 (Nicolet) equipped with a  $30^{\circ}$  specular reflectance accessory. Spectra were recorded in 256 scans with a resolution of 2 cm<sup>-1</sup>.

Raman spectra were measured using a dispersive Raman instrument Nicolet Almega XR with an excitation wavelength of 473 nm and a power of 10 mW. Spectra were collected in 32 expositions with a resolution of 2 cm<sup>-1</sup>.

The X-ray photoelectron spectra were measured on an ESCA 310 (Gammadata Scienta) electron spectrometer equipped with a monochromatized X-ray source of Al K $\alpha$  radiation (hv = 1486.6 eV) and a hemispherical electron analyzer. The pressure of residual gases in the spectrometer chamber was kept below 10<sup>-7</sup> Pa. Photoelectrons emitted in the direction normal to the geometrical surface plane of the sample from the spot of 3 × 5 mm were analyzed. The spectra were fitted using a Gaussian–Lorentzian line shape, a Shirley background subtraction, and a damped nonlinear least-square procedure. The linewidth of peaks [full width at half-maximum (fwhm)] was held constant for all components in a particular spectrum.

#### **Results and Discussion**

Polished metal plates with an area of  $1-2 \text{ cm}^2$  were used as substrates for the deposition of GeNWs. A very thick GeNW layer was developed on the Fe substrate, whereas on the other metal substrates, GeNWs formed fluffy looking deposits (Fig. 1-3) not recognizable by the naked eye. LPCVD performed on cleaned (not polished) commonly used industrial and highly defined AISI 310 stainless steel substrates resulted in GeNW deposits similar to those on the Fe substrates. LPCVD carried out on all substrates roughened with a sandpaper led only to slightly denser deposits. On the contrary, on the freshly roughened steel substrates, thinner deposits were observed.

Using a diamond tip, several long grooves were made on Ta and Mo substrates. Although the grooves did not affect the GeNW growth on the Mo substrate, on the Ta substrate (Fig. 1) a boundary was clearly discernible between a thick deposit of GeNWs in the groove and the low density deposit grown on scratches made by a sandpaper.

Several experiments were performed to synthesize GeNWs on Si and SiO<sub>2</sub> substrates. The GeNW growth on untreated, plain substrates failed. Subsequently, substrates modified with thermally evaporated germanium were used. In this case, scarcely scattered GeNW islands were observed (Fig. 2). As a superficial layer SiO<sub>x</sub> is commonly formed on silicon due to oxidation, another experiment was performed after etching the Si substrate in HF. However, the deposition of GeNWs was not successful either (Fig. 3a). Nevertheless, the thermal evaporation of germanium onto the etched silicon surface before the deposition led to a rapid growth of a brownish deposit with homogeneous texture composed of GeNWs (Fig. 3b).

Independent of the type of substrate, the diameter of the GeNWs ranged from 5 to 20 nm with a length of up to 10  $\,\mu\text{m}$ . Nevertheless,

a) \_\_\_\_\_50 μm





**Figure 1.** SEM micrographs of GeNWs on tantalum substrate: (a) Boundary between thick deposit of GeNWs in a groove [top, enlarged in (b)] and low density deposit of GeNWs clustered on scratches introduced by sandpaper roughening [bottom, enlarged in (c)].

some small differences were found; GeNWs with the smallest diameters (mean value of ~10 nm) were synthesized on the stainless steel substrates (Fig. 4a). The bright-field TEM image shows GeNWs of thickness with the mean value far below the Bohr radius (<20 nm). An irregular thin shell (1–2 nm) on the surface of the GeNWs (Fig. 5a) is composed of amorphous germanium oxide as concluded from the X-ray photoelectron spectroscopy (XPS) results discussed below. Electron diffraction (Fig. 4b) confirmed that the wires are composed of cubic germanium (space group  $Fd\overline{3}m$ , a = 5.623 Å).

Two types of GeNWs were observed using HRTEM: elongated along the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions (Fig. 5). The NWs elongated



**Figure 2.** SEM micrographs of GeNWs on silicon substrate (unetched, Gemodified): (a) Island-looking structure of GeNWs scattered over the whole untreated silicon area and (b) a detailed view of a single island.

along the  $\langle 110 \rangle$  direction (Fig. 5a) are composed of single-crystal germanium without any defects, whereas the other type elongated along the cubic  $\langle 111 \rangle$  direction (Fig. 5b) contains a four-layer hexagonal polytype of Ge, which corresponds to the stacking sequence ABCB (the cubic structure is ABC) also described in Ref. 15.

In the FTIR spectra (not shown here) of GeNW deposits, the following significant peaks were absent: (*i*)  $\nu$ (Ge–Ge) vibration is IR inactive; (*ii*) Ge–O stretching (~980 cm<sup>-1</sup>) was not detected as the amorphous germanium oxide shell is very thin; and (*iii*) the absence of the  $\nu$ (Ge–C) peak (~580–630 cm<sup>-1</sup>) revealed the total separation of germanium and carbon. Carbon traces were present as a graphitelike phase as shown in the Raman spectra (see below). However, most of the carbon material was pumped off as gaseous hydrocarbon molecules in the course of LPCVD.

The XPS analysis of GeNWs on the tungsten substrate showed the presence of two chemical states of germanium. The  $2p^{3/2}$  spectra of Ge are composed of two subpeaks with a binding energy of 1218.5 and 1220.3 eV. The former represents elemental Ge and the latter represents germanium oxide. This fact indicates that GeNWs are oxidized and covered by an irregular thin shell of germanium oxide (Fig. 5a).

In the Raman spectra (Fig. 6), the presence of germanium is proved by an asymmetrical transverse optical (TO) Ge–Ge peak at 290 cm<sup>-1</sup>, which is a characteristic of crystalline germanium. The asymmetry of the peak is caused by a low frequency shoulder, which was identified after deconvolution, as the TO peak of the amorphous germanium with a maximum at 275 cm<sup>-1</sup> and an fwhm of 32 cm<sup>-1</sup>. Such asymmetrical broadening and shift of the TO peak were already predicted and established by several authors.<sup>16-18</sup> The value of the fwhm of the TO peak of crystalline germanium seems to be high



Figure 3. SEM micrographs of GeNWs on silicon substrate (etched): (a) Unmodified by Ge evaporation and (b) modified by Ge evaporation.

(15 cm<sup>-1</sup>); however, in very thin NWs (10 nm and less) as in our case, quantum confinement phenomena should be taken into account. In addition, the Raman spectra show typical D and G peaks at 1361 and 1588 cm<sup>-1</sup>, respectively.<sup>19</sup> Apparently, in the course of the deposition, small graphitic domains were grown, which were built into the island formations as seen on some SEM images (Fig. 1-3). Carbon was also detected by EDX analysis (approximately Ge:C = 1:1).

In the Raman spectra of GeNWs prepared on both types of stainless steel, an additional peak at  $236-241 \text{ cm}^{-1}$  (10 cm<sup>-1</sup> fwhm) is present. The Raman spectra of some samples on W and Ta substrates also showed this peak, distinguished as a shoulder on the TO Ge-Ge peak at 290 cm<sup>-1</sup>. The low frequency region below 250 cm<sup>-1</sup> is occupied by other peaks ascribed to amorphous Ge.<sup>20</sup> However, the peak position of the closest longitudinal optical peak of the amorphous Ge is nearly 20 cm<sup>-1</sup> in distance. Moreover, the fwhm values of those peaks are rather wide  $(40-100 \text{ cm}^{-1})$  to fit our peak. It means that the origin of the peak must be different. Interesting results were obtained by Jang et al.<sup>21</sup> who generated deformations in Ge wafers using indentation tests. By applying various loads, many narrow peaks at 205, 230, 250, and 264 cm<sup>-1</sup> arose (fwhm of the strongest peak at 205 cm<sup>-1</sup> was 8 cm<sup>-1</sup>). After removing the loads, the peaks disappeared in several tens of hours. They tentatively assigned the peaks to the Ge-IV phase, which is cubic with space group  $Ia\overline{3}$ , a = 6.932 Å.<sup>22</sup> Similarly, our peak is placed at approximately 230 to 240  $\text{cm}^{-1}$ . The decrease in peak frequency reveals a weakening of Ge–Ge bonds and the narrow fwhm of 10 cm<sup>-1</sup> manifests a good crystallinity of this new crystallographic phase. A possible candidate is also the hexagonal Ge observed by high resolution transmission electron microscopy (HRTEM) (Fig. 5b). Nevertheless, further studies are necessary.



Figure 4. TEM observations of GeNWs prepared on stainless steel AISI 310 substrate: (a) Bright-field image and (b) corresponding electron diffraction (SAED).



**Figure 5.** HRTEM observations of GeNWs prepared on stainless steel AISI 310 substrate: (a) GeNW elongated along [110] direction (the amorphous germanium oxide shell is indicated) and (b) GeNW elongated along [111] direction contain a four-layer hexagonal polytype of Ge.

*Mechanism of GeNW growth.*— Although the growth mechanism for VLS procedures has been satisfyingly clarified, the initial stage of the noncatalyst growth has not been closely studied so far. An intermetallic concept of the self-catalyst initial stage of GeNWs proposed by Mathur et al.<sup>11</sup> is based on intermetallic nuclei formation. However, we also succeeded in preparing GeNWs on Mo, Ta, and W substrates. Mo and Ta form intermetallic phase(s) with germanium at elevated temperatures of ~700 and 600°C,<sup>12</sup> respectively, which is far above the deposition temperature of 490°C used in our experiments. Moreover, as tungsten does not form any intermetallic alloy with germanium,<sup>12</sup> the elucidation of GeNW growth in the scope of this theory is not interpretable. For those metals, another triggering mechanism has to be considered.

*Noncatalyst mechanism.*— Physicochemical properties of the substrate surface have not been taken into consideration in the theory brought up above. Some conditions have to be fulfilled for the building up of seed nanocrystals on the surface.

First, the incoming atom from the gas phase impinges upon a

bare substrate and adheres to it. It retains a limited mobility until it anchors at a specific surface site. Atoms are gradually captured at the site and form a nucleus nanocrystal.

Second, the surface density of those surface sites has to be appropriately low to nucleate atoms. Otherwise, the incoming atoms get stuck immediately, resulting in a growth of a regular layer.

The nature of the surface site is crucial in the consideration. It can be a defect (for example missing/extra atom at the surface of the substrate material, free bond), imperfections (crystalline edge, face, and grain boundary), or impurities (a surface chemical group) to which the atom can be physically bound due to van der Waals forces. Knowledge of modifying the surface, e.g., what sort of defects, impurities, etc. to generate, would be extremely useful for the fabrication of NW systems. In our work, only specific modifications of some substrates meet the demands (Ge evaporation, grooves made by a diamond tip), whereas others fail (sandpaper roughening). Similarly, Mathur et al.<sup>11</sup> tried to initiate the GeNW growth by



Figure 6. Raman spectrum of GeNWs on stainless steel AISI 310 substrate. Origin of the peak at 240 cm<sup>-1</sup> is discussed in the text.

creating defects using a microindenter. As a result, the indented defects served as nucleation sites for an enhanced growth of nanoflowers (a bunch of GeNWs).

### Conclusions

We successfully synthesized GeNWs using noncatalyst seed LPCVD. The diameters of GeNWs prepared on various substrates were below the Bohr radius (<20 nm). It was also verified that GeNWs grew on Mo, Ta, and W substrates. As the GeNW growth was explained in terms of the theory of intermetallic Ge-Fe alloy in iron substrate, a hypothesis was proposed to clarify this phenomenon for other metals that either do not form intermetallics with Ge (W) at all or do not form intermetallics at the deposition temperature used (Mo and Ta).

The GeNW growth on Si and SiO<sub>2</sub> substrates was promoted by a thin superficial layer of evaporated germanium before LPCVD. This step may introduce a novel approach to GeNW growth on a semiconductive/insulating surface where the use of heteroatoms is inacceptable.

Moreover, a better understanding of (self-)catalyst processes could help to induce specific surface defects or modifications to initiate NW growth. This possibility opens a way to avoid heteroatom catalysts in the production of NW systems.

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