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The synthesis and formation of Ge_xO_y multifacial configurations like nanocrystals using VLS method with two steps temperature mode

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Abstract. This paper outlines shortly the technological process and prilimary experiment results of Ge_xO_y multifacical configurations grown based on VLS method with two steps temperature mode with thick Au metal catalyst layers thicknesses on different Ge surface situation. Their morphologies and structural properties were investigated by SEM, TEM, EDX measurements. The spheres and/or multifacial configurations of Ge_xO_y here are supposed and considered to be Ge_xO_y nanocrystals. The influences of several main aspects of technological factors especially the influence of Au metal catalyst layer thickness on their morphologies have been studied. The formation mechanism of Ge_xO_y multifacial configurations are discussed and proposed.

Keywords: Ge_xO_y multifacial configurations- nanocrystals synthesis, thick Au metal catalyst layer, two steps temperature mode VLS method.

1. Introduction

The nanostructured materials, including the nano thin-films, nanowires (NWs), nanorods (NRs), nanoparticles, and nanocrystals (NCs) played a significant role in the theoretical and practical researches for various applications in nanotechnology and nanodevices [1-3]. To fabricate semiconductor nanomaterials, the top-down and the bottom-up technologies [4] are used. The second one recently is an interesting approach by various methods with the solution phase or gas phase mode [5], for example, by Vapor-Liquid-Solid (VLS) method with one or two steps temperature mode [6-10], by the chemical vapor deposition (CVD) [11], by the plasma-assisted CVD [12], by the laser ablation [13], by Molecular Beam Epitaxy [14], and other methods via simple vapor transport [15]. The VLS growth method could better control over sizes NWs by controlling the sizes of seeds. By using the VLS method we can explain many new interactions [16] and synthesize the different forms and structure of Ge nanomaterials [17]. Recently the Ge_xO_y nanocrystals are very interested. Their synthesis methods as well as the morphologies, structural properties and applications have been reported and discussed intensively [18].

The attention on Ge nanomaterials is mainly owing to their higher intrinsic carrier mobilities, larger bulk excitonic Bohr's radus, bandgap control, compatibility with higher dielectric constant materials that are promising applications for faster switching and high-frequency, field-effect transistor, IR detector, more prominent quantum confinement effects for photoluminescent studies, enabling integration with current semiconductor technology. Ge nanowires (Ge NWs) satisfy criteria of new material with novel structures [9, 11, 12, 15 - 16]. Although many aspects of synthesis and experimental results have been reported on the properties and morphologies of Ge_xO_y nanomaterials, only few works have discussed on synthesis and features of the multifacial configurations, the impacts of Au catalyst layer thickness and the Ge substrate surface states the growth of different sizes Ge_xO_y multifacial configurations.

In this paper, we outline preliminary results of the synthesis process, the impacts of the thick Au catalyst layer and Ge substrate surface states on the growth of Ge_xO_y multi-facial configurations (so-called nanocrystals) by VLS with two steps temperature mode. The growth formation mechanism, structural properties, and the morphologies for the grown different Ge nanomaterials configurations including Ge nanocrystals have also studied and discussed.

2. Experimetal methods

Starting materials were the rough surface Ge slices with n-type, (111) orientation, resistivity about 1 Ωcm these slices obtained from a commercial company. After being cut into several small-size specimens of 5x5 mm, cleaned chemically and vibrated by ultrasonic, all parameters of these specimens are shown in Table 1. All samples have taken to be sputtered with the thick Au layers thickness onto the Ge samples' front side surface in the 10^{-4} - 10^{-5} torr vacuum sputtering equipment. The thickness of Au thin layers thicknesses are about 50 nm and 130 nm. Finally, the samples are thermal annealed in the 10^{-1} to 10^{-2} torr in low vacuum.

Table 1. Technological conditions for growing the Ge_xO_y nanomaterials on different Ge substrate surface states with the thick Au catalyst layers

Groups/ Samples Surface states	Au layer (nm)	Sample label	t_1 (min)	T_1 (^{0}C)	t_2 (min)	t_3 (min)	T_2 (^{0}C)	t_4 (min)
Mechanical polishing surface	130	M6	55	400	75	34	620	60
Deep Chemical etching surface	130	M8	55	400	75	34	620	60
Chemical soft etching surface	130	M10	55	400	75	34	620	60
Initial rough surface	130	M12	55	400	75	34	620	60

3. Exeprimental results

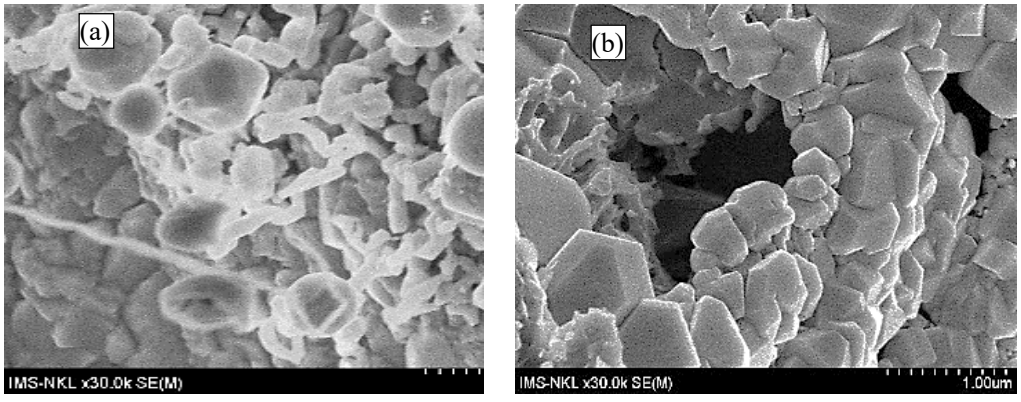

Figure 1. FESEM micrographs of Ge_xO_y NCs configurations grown on the mechanical polishing surface M6 sample with thick Au catalysis layer of 130 nm.

The obtained experimental results for growths of the Ge_xO_y multifacial configurtions, so called nanocrystals (NCs) on the different Ge substrate surface states at different Au catalyst layers thicknesses can be seen from Figure 1 to Figure 6. Figure 1 shows the multifacial configurations grown on sample M6. The technological conditions for growing nano configurations are outlined in Table 1. The sizes are about 500 nm-700 nm with spheres and NCs. There are some NNWs, NRs also grown (Figure 1a). The etching phenomenon due to the effect of thick Au catalyst layer also observed (Figure 1b).

Figure 2 shows the NCs grown on M8 sample with deep chemical etching surface sample. The size of NCs is about 1 µm to 2 µm with 130 nm Au catalyst layer, here there were no NWs grown that can be found.

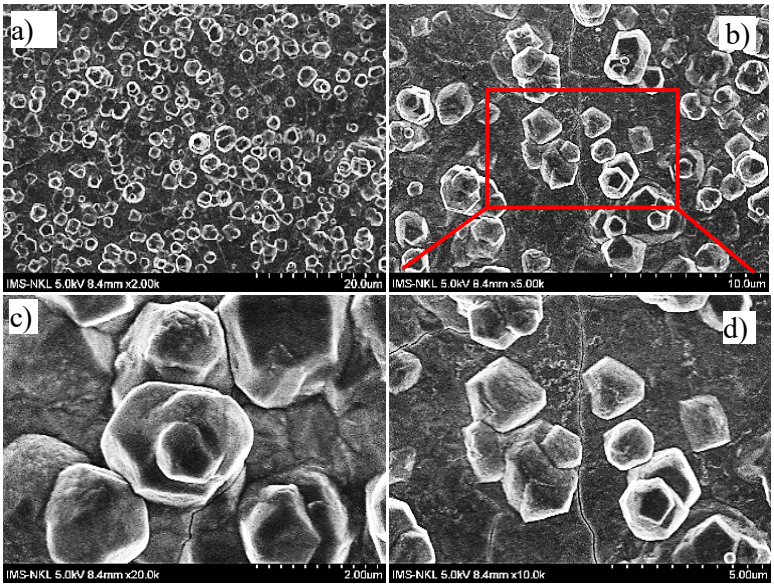

Figure 2. FESEM micrographs of the multifacial NCs configurations grown on deep chemical etching surface M8 sample with thick Au catalyst layer of 130 nm.

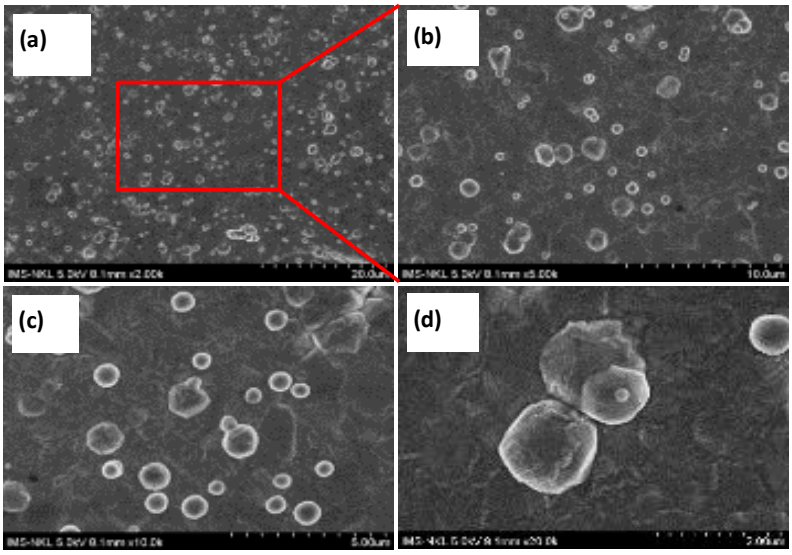

Figure 3. NCs configurations grown on M10 samples with the chemical solft etching surface in the case of 130 nm Au catalyst layer thickness.

Figure 3 shows SEM images of Ge_xO_y NCs grown on chemical soft etching surface M10 sample with 130 nm Au layers. Here there are only NCs configurations of Ge_xO_y grown with a big size of

about 1.5 µm to 2 µm for chemical etching surface samples. The FESEM of sample M12 is shown in figure 4.

Figure 5 shows the HRTEM micrographs of a multifacial nano configuration (NCs) grown on M6 sample with cross-sectional images obtained at its edge. The typical multifacial NC configuration is shown in Figure 5a with a cover, a shell layer with the size of about 5-6 nm, the structure of shell layer is morphorous as shown in Figure 5b, 5e). The core of NC is a crystalline structure (Figure 5d) with insert HR–TEM image from the indicated box. The inset shows the corresponding pattern recorded along with the (200), (111) and (022) orientation. The atoms layer space is 0.334 and 0.294 nm as shown in Figure 5c).

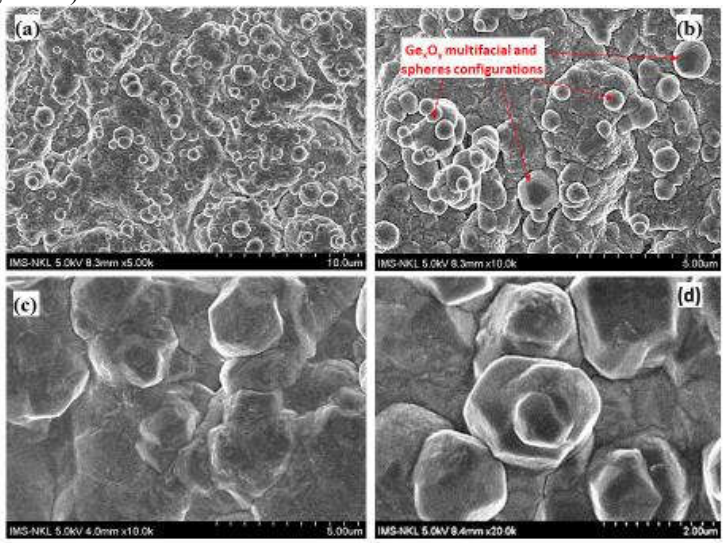

Figure 4. FESEM micrographs of Ge_xO_y NWs configuratiuons grown on sample M12 in the case of the initial rough Surface sample with 130 nm Au catalyst layer at different magnifications.

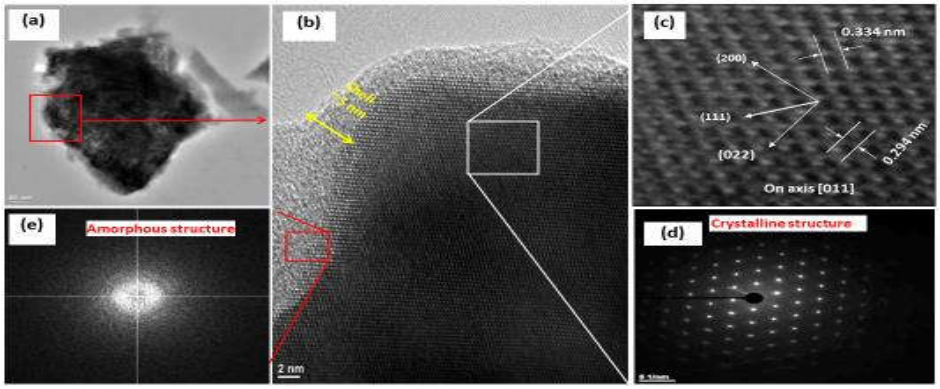

Figure 5. HRTEM images of an NC configuration on M6 sample with the mechanical polishing surface sample. NC has a shell with crystalline structure (b, c, d), and amorphous shell layer structure with a size about 5 nm (b, e).

4. Discussion

As known, A nanocrystalline (NC) material is a polycrystalline material with a crystallite size of only a few nanometers definitions vary, but nanocrystalline material is commonly defined as a crystallite (grain) size below 100 nm. Grain sizes from 100–500 nm are typically considered "ultrafine" grains. Nanocrystalline materials can be prepared in several ways: Solid-state processing [21].

About nanocrystals of the nano Ge_xO_y configurations grown on the different samples with the different Ge substrate surface states at 130 nm Au catalyst layer thickness in our case, the growth of

NCs strongly depending on the Au catalyst layer thickness and also on Ge substrate surface situations which relate to number of defects, lead to different sizes and morphologies of multifacial configurations, i.e. the surface defect situation is strongly determined by the sizes and morphologies of multifacial nanomaterials configuration (NCs). The influences of the Ge substrate surface states on the formation and growth of nano materials configuration are not found so much before [13]. After thermal annealing, the sizes of Au droplets could be formed almost equally, the NWs can be grown [10], but for thicker Au catalyst layer with the defective surfaces of Ge substrate, here only NCs configurations are grown. Here we suppose that the chemical-physical reactions, relative compositions of Ge, O and the role of Au catalyst in the thick Au layer and/or Au droplets behaviors these factors affect strongly to the nanoseeds formations as well as the orientations of nanoseeds where the NWs growth are not occurred.

The growth mechanism of the NCs could be supposed as follows: During the thermal annealing at T_1 and growing T_2 temperature above the Eutectic temperature (361°C) of Au-Ge system, firstly Au droplets then Au/Ge/O clusters are formed. Depending on the technological conditions, the dissolution of Ge and O atoms into Au droplets could reach the supersaturating level or not. For the Au layer of 130 nm, the large Au droplets forms after annealing process (T_1) and in growing process (T_2), the Au/Ge/O configurations are formed but it is hard to reach suppersaturation levels, the NWs seeds and their orientations are also hard formed, in additional the NCs could be explained by the lack or poor of Oxygen environment that could lead to hard formation of NWs seed in the Au/Ge/O clusters, consequently instead of NWs, NRs a grown, the spheres and/or multifacial configurations (NCs) grown as shown in Figures 1-4 .

5. Conclusion

This paper outlined the developments of technological processs using the thermal VLS method with two steps temperature mode to grow and investigate the several features of the Ge_xO_y multifacial configurations so called NCs on different Ge substrate surface situations. When the thickness of the Au catalyst layer influences on the forms and sizes of NCs grown in all cases of different Ge substrate surfaces. The formation of NCs could be supposed due to the large Au droplets and Au/Ge/O clusters formed after thermal treatment in the case of thick Au layers and due to the lack of oxygen atoms (O) being in the Au/Ge/O clusters for creating NWs seeds and/or not enough Ge and O atoms diffused or absorpted into big Au droplets, the supersaturating level is not or hard to reach in large Au/Ge/O clusters, then the nucleation of the nanowires seeds will not also be formed, then the big NCs configurations will be grown. The formation mechanism of NCs is still ambiguous and need to be researched more in the future.

Acknowledgments

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