Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 692-693

P-13-2

Effects of Cu Catalyst and Water Vapor on the Growth of Ge-GeO$_x$ Core-Shell Nanowires via the Carbothermal Reduction of GeO$_2$ Powders

Wei-Long Lo, Ting-Jui Hsu and Wen-Tai Lin

Department of Materials Science and Engineering, National Cheng Kung University,
Tainan, Taiwan, 70101, Republic of China
Phone: 886-6-2757575 Fax: 886-6-2745985 E-mail: wtlin@mail.ncku.edu.tw

1. Introduction

Germanium nanowires (NWs) have hold promises for applications in electronic nanodevices. However, Ge is sensitive to oxidation and thus suffers from the water corrosion in air [1]. Passivation of the surface of Ge NWs is one of the important processes for realizing a high-performance device. Several types of sheathed Ge NWs has been grown [2-6]. The fabrication methods include vapor-liquid-solid (VLS) process [2,3], vapor-solid (VS) process [4,5] and oxide-assisted growth [6].

The VLS process is an important way to grow Si and Ge NWs, where an expensive Au catalyst is generally utilized [2]. Copper is a new interconnect material in semiconductor integrated circuits. It was reported that Cu contamination can cause the growth of Si NWs via the VLS process at 550˚C [7]. However, another report showed that the Cu-catalyzed growth of Si NWs at 500˚C is via the VS process [8]. Therefore, the mechanisms for the Cu-catalyzed growth of semiconductor NWs remain to be further understood.

The water vapor has been used as an oxidizing agent to promote the growth of various oxide NWs [9,10] because it can produce atomic oxygen at an elevated temperature. However, the effects of co-produced atomic hydrogen from water on the growth of NWs remain to be explored yet. In the present study, the effects of Cu catalyst and moist Ar on the growth of Ge-GeO$_x$ core-shell NWs (Ge-GeO$_x$ NWs) via the carbothermal reduction of GeO$_2$ powders at 1100˚C were reported. In addition, the mechanisms for the growth of Ge-GeO$_x$ NWs were discussed.

2. Experimental

Mixed powders of GeO$_2$(99.999%)/graphite(99%) with the weight ratio of 1:1 were prepared. The mixed powders, about 1.2 g, were loaded into an alumina boat. Cu films 10-50 nm thick were deposited onto Si(100) substrates in an electron beam evaporation system. The Cu-coated Si substrates were put on the centre of an alumina boat. Then the alumina boat associated with the substrates was loaded into a tube furnace. The growth of NWs was performed at 1100˚C for 60 min in flowing Ar at a flow rate of 100-300 sccm. In some cases a crucible containing 1 ml of DI water was placed in front of the alumina boat. After growth the samples were cooled in air. The microstructure of the samples was observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), both of which are equipped with a field emission gun. The chemical compositions of the samples were analyzed using TEM/energy dispersive spectrometer (EDS).

3. Results and discussion

At 1100˚C in dry Ar, significant NWs were grown on the Cu-coated Si substrate, while almost no NWs occurred on the bare Si substrate. The NWs are composed of a [111]-oriented Ge core and an amorphous GeO$_x$ shell as shown in Fig. 1. In addition, a spheroid is present at the tip of Ge-GeO$_x$ NWs. TEM/EDS data in Fig. 2 shows that the spheroids are composed of Cu, Ge, and O. The eutectic temperature of CuGe alloy is 644˚C. At 1100˚C the spheroid can be in the liquid state, revealing that the growth of Ge-GeO$_x$ NWs follows the VLS process.

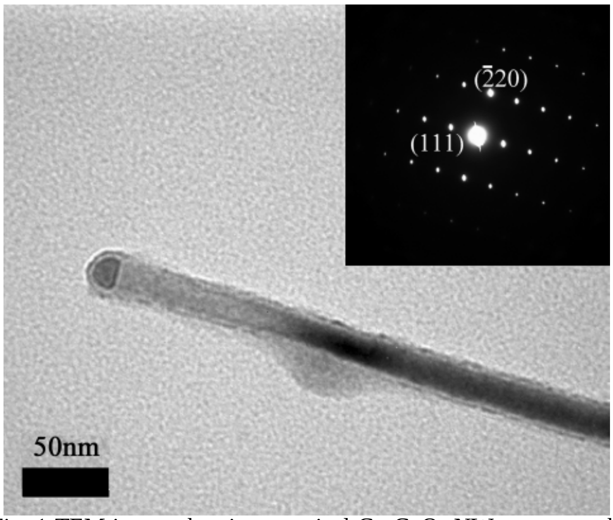

Fig. 1 TEM image showing a typical Ge-GeO$_x$ NW grown on the Cu-coated Si substrate in dry Ar at 200 sccm.

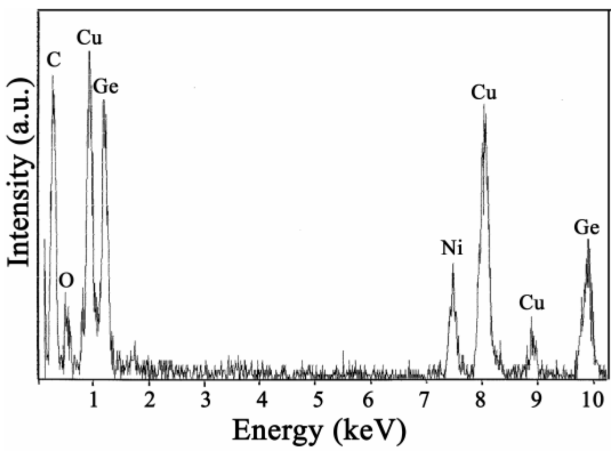

Fig. 2 TEM/EDS spectrum of the spheroid at the tip of the Ge-GeO$_x$ NW in Fig. 1.

The amount of Ge-GeO$_x$ NWs increased with increasing the thickness of Cu films from 10 to 30 nm as shown in Figs. 3 and 4. This result indicates that the nuclei of Ge-GeO$_x$ NWs increase with the thickness of Cu films. However, for the substrates with the Cu film 50 nm thick the Ge-GeO$_x$ NWs tended to agglomerate like an island. Nevertheless, the present study showed that Cu can indeed serve as a catalyst to enhance the growth of Ge-GeO$_x$ NWs via the VLS process.

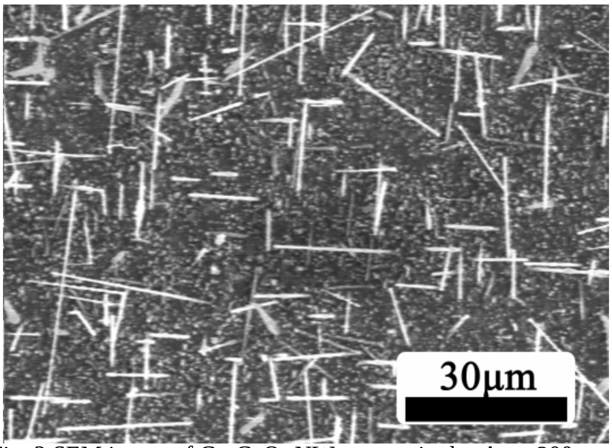

Fig. 3 SEM image of Ge-GeO$_x$ NWs grown in dry Ar at 200 sccm on the Si substrate coated with a Cu film 10 nm thick
.

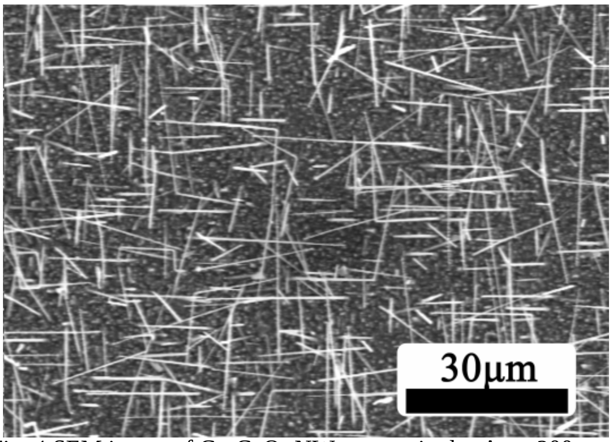

Fig. 4 SEM image of Ge-GeO$_x$ NWs grown in dry Ar at 200 sccm on the Si substrate coated with a Cu film 30 nm thick.

In the present study, therefore, the reactions for the Cu-catalyzed growth of Ge-GeO$_x$ NWs via the VLS process can be proposed as follows:

$$GeO_2 + C \rightarrow GeO(g) + CO \quad (1)$$
$$2GeO(g) + (2-x)Cu \rightarrow Cu_{2-x}Ge(liq.) + GeO_2 \quad (2)$$
$$GeO_2 + 2CO \rightarrow Ge + 2CO_2 \quad (3)$$

The vapor point of GeO(g) is 710˚C. First, GeO(g) produced by the carbothermal reduction of GeO_2 powders at 1100˚C flows with the carried Ar gas and then reach the Si substrate to react with Cu films to form CuGeO droplets containing GeO_2. As the CuGeO droplets are saturated with GeO_2 species, GeO_2 nuclei precipitate on the lower surface of the droplets and then reduced by CO to form a Ge-GeO$_x$ core-shell structure. As Reactions (1), (2), and (3) go on, the Ge-GeO$_x$ core-shell structures grow up to form epitaxial Ge-GeO$_2$ NWs and finally the CuGeO droplets are lifted away the Si substrate.

When introducing the water vapor into flowing Ar, more Ge-GeO$_x$ NWs were grown as shown in Fig. 5. It is conceived that the atomic oxygen and hydrogen from the water vapor serve as oxidizing and reducing agents, respectively, to enhance the growth of Ge-GeO$_x$ NWs. More detailed studies are under way.

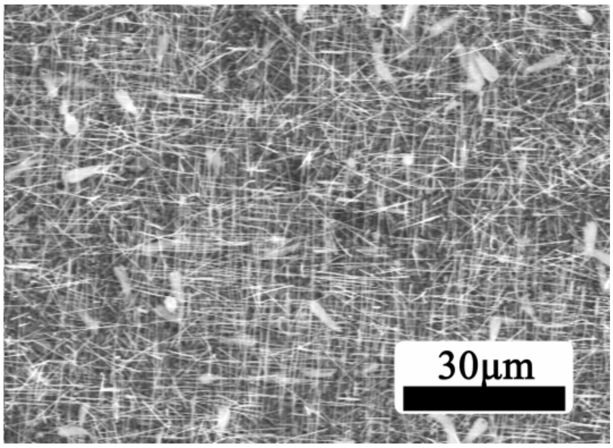

Fig. 5 SEM image of Ge-GeO$_x$ NWs grown in moist Ar at 200 sccm on the Cu-coated Si substrate.

4. Conclusions

Cu-catalyzed growth of Ge-GeO$_x$ NWs via the VLS process was observed upon the carbothermal reduction of GeO_2 powders in dry Ar at 1100˚C. Introducing the water vapor into flowing Ar further enhanced the growth of Ge-GeO$_x$ NWs, possibly because the atomic oxygen and hydrogen from the water vapor serve as oxidizing and reducing agents, respectively.

Acknowledgements

This work was sponsored by the Republic of China National Science Council under Contract No. NSC95-2221-E-006-114.

References

[1] D. Wang, Y.L. Chang, Q. Wang, J Cao, D.B. Farmer, R.G. Gordon and H. Dai, J. Am. Chem. Soc. **126** (2004) 11602.
[2] Y. Wu and P. Yang, Appl. Phys. Lett. **77** (2000) 43.
[3] Y. Huang, J. Lin, J. Zhang, X.X. Ding, S.R. Qi and C.C. Tang, Nanotechnology **16** (2005) 1369.
[4] J.Q. Hu, X.M. Meng, Y. Jiang, C.S. Lee and S.T. Lee, Adv. Mater. **15** (2003) 70.
[5] C.Y. Ko and W.T. Lin, Nanotechnology **17** (2006) 4464.
[6] Y.F. Zhang, Y.H. Tang, N. Wang, C.S. Lee, I. Bello and S.T. Lee, Phys. Rev. B **61** (2000) 4518.
[7] M. Nagai, Electrochem. Solid-State Lett. **10** (2007) H43.
[8] Y. Yao and S. Fan, Mater. Lett. **61** (2007) 177.
[9] Y.K. Tseng, I.N. Lin, K.S. Liu, T.S. Lin and I.C. Chen, J. Mater. Res. **18** (2003) 714.
[10] K. Hong , W. Yiu, H. Wu, J. Gao and M. Xie, Nanotechnology **16** (2005) 1608.