

***In situ* investigation of self-catalyzed purity Copper nanowire growth through seed-mediated synthesis**

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Abstract

In the initial stage of the nanomaterials nucleation system, seed crystal induces critical reaction of the atom aggregated droplet nucleation could be the decisive growth behavior of nanostructures. Even though the dynamic mechanism of one-dimensional material has been studied for several decades less of research investigated the complete nucleation process of the nanomaterial, owing to the challenge of the uncontrollable nucleation barrier and unexpected interregional crystallization process. In this work, we investigated the synthesis mechanism of high purity copper (Cu) nanowires without any catalyst and defect induced from the initial stage of the Cu droplets cluster supersaturation to the Cu nanowire outgrowth, following a simple one-step procedure by using the copper grid with a heating system in the ultra-high vacuum (UHV) environment (1×10^{-7} pa) under 700 °c. During the vacuum vapor deposition (VVD) process, the inertness of amorphous carbon (a-C) film provides an intriguing support for heterogeneous nucleation reaction. By raising the concentration of Cu atoms on hetero surface, the purity Cu nanowire growth by the base nuclear seed with specific supporting growth plane <110>. The mechanism of self-catalyzed purity Cu nanowire growth were based on the observation of different stage growth dynamic with high resolution transmission electron microscope (HR-TEM) analysis, and high resolution chemical analysis provided by electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS). Those results shown both anisotropic properties of lowest surfaces free energy and the seed crystal behavior drives the high production purity Cu nanowire outgrowth with the controllable aspect ratio in the VVD process.

1. Introduction

In industry, most synthetical mechanisms of Cu nanowire application devices were reported by the use of chemical precursor as the catalyst.^[1] Owing to the diameter control of catalyst particle and the hetero surface conditions could affect to each other^[2], the synthesis accuracy of nanowire growth could be confined with the catalyst guided. In addition to few problems occurred, such as the requirement for further separation of the catalyst material and the precise control of environmental parameters, during the use of cata-

lyst. Moreover it has been recently shown the normalize synthesis technological of catalyst-free method.^[3]

Here, we successfully prepared the purity Cu nanowire with controllable aspect ratio and no oxide doping. Reactant supplement through the thermal evaporation of the system follow the internal anisotropic surfaces energy of the Cu nanowire. According to the limit critical size and activation energy of Cu nucleation reduced, purity Cu nanowire could be formed on the graphite member.^[4]

Those results have been investigated in the in situ TEM observation and given the valuable information about the kinetics study of Cu atomic transportations through the nanowire outgrowth, shown the uncommonly nucleation process on the a-C lacey film from the initial stage of the Cu seed crystallization. Adverse molten reaction between Cu and a-C lacey film raise the nucleation ability of Cu supersaturation and helps the crystallization for each nanocrystal form different interaction of the anisotropic properties. In order to understand the synthetical mechanisms accurately, the integral explanations in this work were reported by the high resolution chemical analysis of EDS, EELS and the microstructure analysis of HRTEM from different orientation compared the molecular dynamics simulation modelling of the Cu nanowire growth mechanism results.

2. General Instructions

In this work, vacuum thermal annealing active the Cu source divided into evaporation process and crystallize to the seed crystal by droplet contact-induced on the a-C lacey film of the unit copper grid through the thermal annealing process and performed inside an ultrahigh vacuum (UHV) system. Via the in situ TEM observation form different Cu restructures is shown in Fig 1a-c, the nucleation dynamic of nanowire growth could be obviously distinguished as the main active reaction during the VVD process.

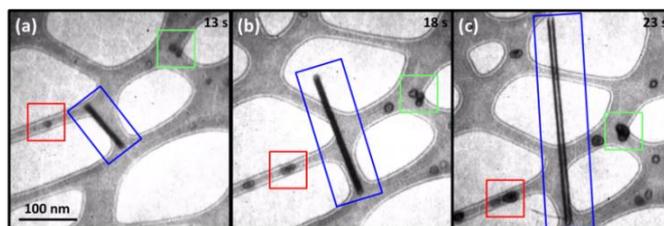


Fig 1. Various characteristic Cu crystallization via in situ TEM observation.

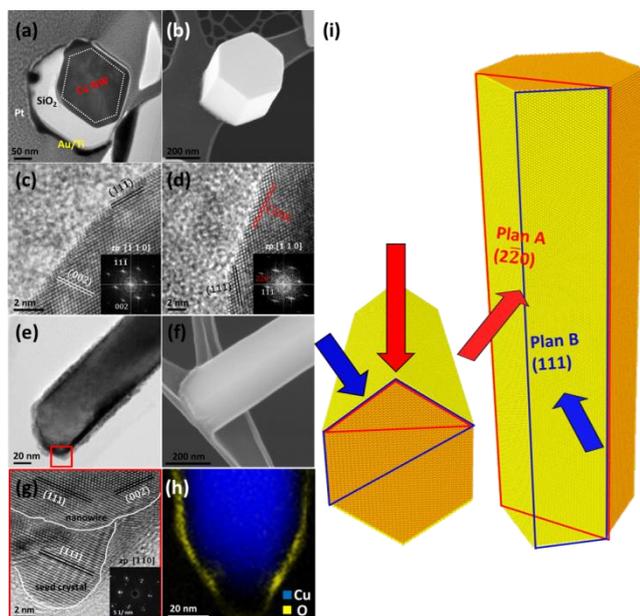


Fig 2. Modelling the Cu nanowire with SEM · HRTEM and EELS analysis from different observed orientation.

For the understanding of the Cu nanowire synthesis mechanism, we provide complete details by TEM structure analyze technique of the Cu nanowire from different observed orientation. The core-section sample of the Cu nanowire is produced by e-beam supporting and focus ion-beam (FIB) technique, the TEM images showed the hexagonal column morphology with symmetry $\langle 111 \rangle$ and $\langle 200 \rangle$ phase in Fig 2a, c and d. SEM images of single crystal Cu nanowire morphology are shown in Fig 2b and f. As the seed crystal induced the Cu nanowire outgrowth at the initial stage of crystallization, we focused on the base side of a high purity Cu nanowire shows a clear junction interface with a-C film in Fig 2e and the high resolution image of the bonding plane were both (111) and (200) phase in Fig 2g. EELS mapping in Fig 2h confined with the purity Cu supported the findings of the HRTEM image on the location of the nucleation seed. The Cu nanowire geometry structure could be clearly confirmed as the modelling for the molecular dynamics simulation method shows in Fig 2i.

Molecular dynamics simulation provided the environmental conditions and chemical potential between Cu and carbon molecules. The integral simulation of the synthesis mechanism were following the atomic aggregation in Fig 3a to the Cu droplets cluster supersaturation in Fig 3b then the Cu nanowire growth in Fig 3c, the inertness of amorphous carbon (a-C) film provide an intriguing support for heterogeneous nucleation reaction. With the high thermal treatment as the disadvantage of the crystallization the source supplement in the system enhanced the surface diffusion on the $\langle 111 \rangle$ driven by the concentration gradient of Cu molecules on the hetero surface, the purity Cu nanowire growth by the base nuclear seed with specific supporting grow plane

$\langle 110 \rangle$ as the in situ TEM observation from Fig 3d to 3f.

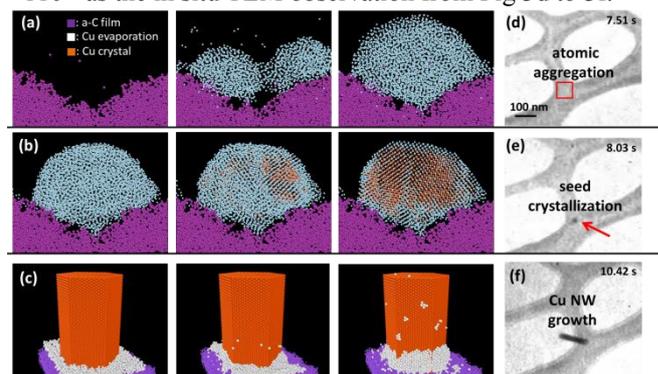


Fig 3. Mechanisms dynamic report of the Cu nanowire outgrowth through the Cu atom aggregation, nucleation and nanowire growth on the a-C film, created by molecular dynamics simulation.

3. Conclusions

In this study, we focused on the initial stage of the Cu nanowire nucleation via catalyst-free methods in the annealing process of the UHV environment (1×10^{-7} pa). We completely investigated the purity single-crystal Cu nanowire outgrowth on the a-C lacey film without catalyst need and defect induced. Based on the inertness of a-C film supported, the heterogeneous nucleation of Cu nanowire on the hetero surface was induced by the nuclear seed which is also the critical issue of the Cu nanowire outgrowth. The driving force of the Cu nanowire outgrowth was limited and control by the Cu atom deposition concentration through the VVD process. Our report of growth dynamics from the in situ movie were combined with the HRTEM structure analyze, and chemical analyze (EELS and EDS), those results point on the anisotropic properties of lowest surfaces free energy (surface diffusion from the $\langle 111 \rangle$ to the $\langle 110 \rangle$ growth plane) and the seed crystal behavior drives nucleation dynamics of the high production purity Cu nanowire outgrowth.

Acknowledgements

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