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Electron beam induced growth of silver nanowhiskers

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ABSTRACT

In this paper we report an electron beam induced rapid (up to several tens of nm/s) growth of silver nanowhiskers from silver nanowire networks coated with TiO_2 by sol–gel method. Different growth conditions are tested and it is demonstrated that growth is optimal for samples with the film thickness in the range 50–200 nm and previously annealed at 400 °C for 5–10 min. Growth mechanism is attributed to cooperative effect of several factors including diffusion of Ag into TiO_2 matrix during annealing, electromigration of Ag atoms caused by strong electric field, and presence of mechanical stresses at interfaces enhanced by thermal expansions due to local heating under e-beam illumination.

1. Introduction

Spontaneous growth of one-dimensional (1D) solid structures with the diameter ranging from several nm to several microns and the length reaching sometimes several mm known as whiskers, was often observed on the metallic coatings with relatively low melting point such as tin, cadmium, zinc in ambient conditions (see, e.g. [1,2]).

Besides the growth in ambient conditions, metal whiskers were observed to grow when exposed to specific environment. Pronounced formation of silver whiskers was observed in gaseous sulphur containing environment [3]. Aluminium whiskers grew with a high rate in certain narrow range of temperatures [4]. Whisker growth rate can be relatively high with the incubation period from several days to several years.

The problem of metal whisker growth was widely discussed starting from 1940' [5,6]. Nowadays, real-time observations of whiskers growth can be done with advanced experimental facilities, e.g. using the focused ion beam (FIB) and scanning electron microscopy (SEM) techniques, see the results by Jadhav et al. [7] for micron diameter scale tin whiskers. Moreover, irradiation of certain specimens with electron beam during routine observation in electron microscopes can facilitate the growth of whiskers. E.g. Edmondson [8] demonstrated electron beam induced growth of silver whiskers from zeolites chemically loaded with silver ions.

One of the characteristic features of the whisker growth is their extrusion from the base material [9]. Presence of intrinsic compressive mechanical stresses was named as one of the main conditions and the driving force of spontaneous growth. This premise was exploited in various models of whisker growth. The concepts and models of whiskers growth were proposed using different approaches: dislocation based models [10–12], models of polycrystalline grain recrystallization [13], diffusion related models [14–17]. Distribution of mechanical stresses in the coating was modelled and mapped to whiskers growth [18]. There were also attempts to link metal whiskers growth with the strong electric field [19]. To the best of our knowledge, there is no general and comprehensive model explaining growth of whiskers at given conditions and in connection to their intrinsic structure.

Silver nanowires (AgNWs) have been the focus of many recent research projects of fabrication of transparent electrodes for solar cell, touch panel and flat-panel display applications [20]. The AgNW random network is interesting due to its high electrical conductivity and optical transmittance [21,22]. The electrodes can be readily prepared by simple and scalable methods such as spin coating, rod coating, and spraying from a AgNW-s dispersion [23,24]. AgNWs are also promising components in fabrication of flexible transparent electrodes due to high fatigue resistance of NWs [21,25]. However, such electrodes can fail due to corrosion of AgNWs exposed to ambient conditions, which adversely affects the conductivity of AgNW network [22]. Another reason of the electrode failure is that AgNWs are instable at elevated temperatures caused, e.g. by electrical current [26]. Coating of AgNWs

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network with thin oxide layer could potentially protect them from the corrosion [27]. Moreover, it was recently demonstrated that TiO_2 shells increase thermal stability of individual AgNWs [28].

In this paper we demonstrate the electron beam-induced growth of silver nanowhiskers observed in real-time in SEM on the surface of a TiO_2 layer that covers AgNWs network. Growth conditions are systematically studied and possible growth mechanisms are discussed.

2. Materials and methods

2.1. Preparation of TiO_2-coated AgNWs network

A sol–gel route was utilized for titania (TiO_2) coating synthesis. Titanium(IV) butoxide (Alfa Aesar 99%) was used as sol precursors for subsequent coating of Ag NWs networks. Three different TiO_2 precursors were prepared: with HCl as catalyst, with HNO_3 as catalyst, and without any catalyst.

General preparation procedure was similar for all three cases. The sol precursor was obtained by a partial hydrolysis and condensation of titanium(IV) butoxide with water, and using ethanol as the solvent. The mixture of water, ethanol and if applicable the catalyst was added to titanium(IV) butoxide, and the sol was stirred for 1 h at room temperature. The molar ratio of water to titanium(IV) butoxide was 0.5 and the molar ratio of the catalyst to titanium(IV) butoxide was 0.05. The ratio of titanium(IV) butoxide/ethanol was set to 34/66 by weight. Water and ethanol were removed by rotator evaporator (Büchi R-114) to decelerate the hydrolysis and condensation reaction of the sol precursor, and the concentrated sol was dissolved in hexane (10 wt%). The solution was kept overnight before deposition of titania layers onto AgNW network. Since titanium(IV) butoxide is sensitive to water, ethanol and hexane were dried using CaH_2 and distilled prior to utilization.

AgNWs network was prepared by depositing a droplet of AgNWs-containing ethanol solution (Blue nano, 1 mg/mL) onto silicon (100) substrates (10 mm × 10 mm) by spin coating at 1000 r/min for 60 s. Samples with AgNW networks were dried at 120 °C for a few minutes to remove the solvent. TiO_2 precursors were spun at 3000 r/min for 60 s onto the AgNWs network to form TiO_2 sol layer.

2.2. Thermal treatment

Ten samples were prepared with HCl as catalysts and two annealing series were carried out at different temperatures and

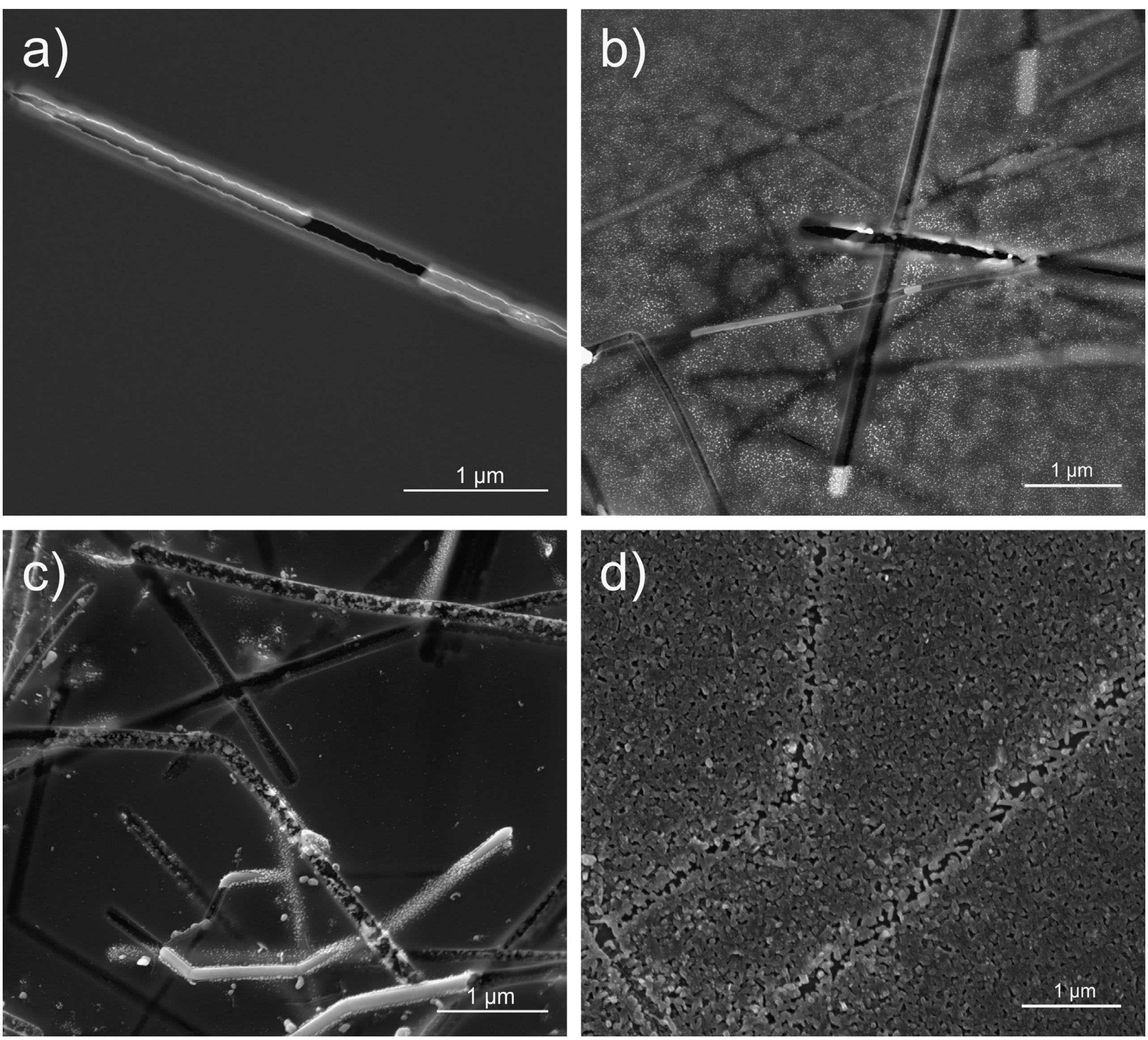

Fig. 1. SEM image of AgNW network on silicon substrate covered with TiO_2 layer annealed at (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 600 °C.