Lowered Melting Point of Polyvinyl Pyrrolidone Bound 1D Ag Nanowires

Akihiro Tomioka 1, Kenji Ozasa 1 and Masato Kawabata 1

¹ Osaka Electro-Communication University, 18-8 Hatucho, Neyagawa, Osaka 572-8530, Japan

Ag nanowires draw an increasing attention as a material with superior electrical conductance: with adequate printing on a transparent glass or plastic film, they bring about a semitransparent electrode, which has a demanding need in touch panel devices in "smart phones" and portable "tablets".

Ag nanowires were grown by an energy-conserving solution process in the present study via polyol-assisted scheme: ethylene glycol (EG) served both as reducing agent and as solvent. EG enabled the chemical reaction performed up to its boiling point (195°C). We utilized Au nanoparticles as crystallization seeds, based on the fact that Ag and Au have similar crystal lattice spacing. Polyvinyl pyrrolidone (PVP), reported to attach Ag crystal in a facet-selective manner and thereby to act as structural directing agent, was used to facilitate the preferential formation of 1D Ag nanowires on Au nanoparticle seed (purple color appearance). The elongation of 1D Ag nanowires was easily ascertained by the color change to turbid gray (greenish or yellowish, depending on the nanowire length). The elongation time was dramatically shortened above 160°C, indicating that PVP serves as catalyst to facilitate the elongation of nanowires. Thermal energy at 160°C should be equal to the activation energy of PVP binding to Ag nanowire side face.

The resulting Ag nanowires were centrifuged and resuspended in 2-propanol twice in order to wash out the reagents, and deposited on Si wafers. Morphology of Ag nanowires was observed by SEM, before and after successive heat treatment at 200° C, 230° C, 250° C, 270° C and 300° C. As deposited, Ag nanowires showed straight profile over 5μ m, with sharp well-defined edges. Some of the nanowires, or only portions of single nanowire, became spherical (droplet-like) and the ratio was increased monotonically with increasing temperature. All the nanowires became spherical at 300° C, indicating that the melting point (MP) was 200° C - 300° C, greatly lowered from 962° C of the bulk Ag MP.

Even Ag nanowires with similar diameter (60-70 nm) preserved the same variation of the MP, suggesting that nanowire diameter did not govern the MP. The lower MP is not due to the Ag-Si eutectic because Si wafer has a naturally formed SiO_2 surface layer (~3 nm thick) which inhibits Si atom incorporation into Ag nanowires. For example, Au (MP $1064^{\circ}C$) and Si (MP $1414^{\circ}C$) forms eutectic whose MP can be as low as $370^{\circ}C$, and Ag-Si eutectic also shows similar MP: this is not the case with Ag nanowires on stable oxide.

Possible origin may be PVP polymers tightly bound to the nanowire surface: catalytic behavior of PVP suggests a large binding energy of PVP, which will modulate the surface energy of Ag nanowires. Flexible C-C single-bond PVP backbone may induce a structural variation among tightly bound PVP's, leading to surface energy variation along a nanowire and among different nanowires.