Unexpected Oxidation Behavior of Cu Nanoparticles Embedded in Porous Alumina Films Produced by Molecular Layer Deposition

Yong Qin,†,* Yang Yang,† Roland Scholz,† Eckhard Pippel,† Xiaoli Lu,† and Mato Knez†,*

†Max Planck Institute of Microstructure Physics, Weinberg 2, Halle 06120, Germany
‡Laboratory for Nanotechnology, Institute of Microsystems Engineering (IMTEK), Albert-Ludwigs-University Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany

Supporting Information

ABSTRACT: This work reports an unexpected oxidation behavior of Cu nanoparticles embedded in porous Al2O3 confinements that are produced by annealing alumina (an organic–inorganic hybrid material) deposited by molecular layer deposition. An oxidation of such encapsulated Cu nanoparticles by annealing in air produces Cu oxide nanoparticles attached to the outer surface of the hollow Al2O3 nanostructures, which is in strong contrast to bare or compact, nonporous Al2O3-coated Cu nanoparticles, which result in hollow oxide nanospheres or do not undergo oxidation, respectively. The conversion from encapsulated Cu to supported oxide nanoparticles is explained by a concerted pore-assisted diffusion and oxidation mechanism. The micropores in the films, having diameters of several angstroms, permit a selective out-diffusion of Cu atoms and prevent the inward diffusion of oxygen. The subsequent oxidation occurs at the pore entrances, which work as multiple nucleation sites for the formation of oxide nanoparticles with a small size and good dispersion.

KEYWORDS: Molecular layer deposition, atomic layer deposition, diffusion, porous film, supported nanoparticles, Kirkendall effect

Oxidation of bare metal nanoparticles or nanowires usually results in hollow nanospheres or nanotubes. For example, Yin et al. reported that CoO hollow nanocrystals were formed by the reaction of Co nanocrystals with oxygen.1 Nakamura et al. investigated the formation of hollow Cu2O and Al2O3 nanoparticles by oxidation of Cu and Al nanoparticles in air, respectively.2 Chang et al. observed that copper nanowires, once oxidized, produce Cu oxide nanotubes via direct oxidation in air.3 The formation mechanism of such hollow nanostructures was commonly explained with the nanoscale Kirkendall effect, the difference in diffusion rates between the metal and the oxygen.4–7 In contrast, metal particles coated with compact, nonporous films such as SiO2 and Al2O3 exhibit remarkably high oxidation resistance, because the insulating films behave as a barrier layer for the diffusion of both oxygen and metal.5–8 For example, Hakim et al. reported that a coating of nonporous Al2O3 even with a thickness of several nanometers allowed passivation of Fe nanoparticles.9 In this work, we show an unexpected oxidation behavior of metal nanoparticles embedded in a new type of porous film. Cu nanoparticles confined in porous Al2O3 nanotubes or coated with porous Al2O3 films produced by molecular layer deposition (MLD) can be oxidized to produce Cu oxide nanoparticles attached to the outer surface of hollow Al2O3 nanostructures by annealing in air. The conversion from encapsulated Cu to oxide nanoparticles attached to the outer surfaces of the hollow Al2O3 nanostructures is explained by a concerted pore-assisted diffusion and oxidation mechanism.

For the preparation of Cu nanoparticles embedded in porous Al2O3, CuO nanowires are first prepared by heating Cu substrates in air for 2 h as described previously.10,11 Bare Cu grids (3.05 mm in diameter) were used as substrates for convenience and directly applied for subsequent analysis after every process step. Subsequently, deposition of an organic–inorganic hybrid material (alumina) on the CuO nanowires was carried out by MLD with trimethylaluminum (TMA) and ethylene glycol as precursors at 100 °C with a deposition rate of 2.2 Å per cycle.12 During MLD, glycol was heated to 45 °C and TMA was kept at room temperature. Figure 1a shows a transmission electron microscope (TEM) image of CuO nanowires coated with a 37 nm thick alumina film. The diameters of the CuO nanowires range from 30 to 150 nm and their lengths reach 10 μm. The conformal alumina layer can be clearly observed from the magnified image shown in Figure 1b. Note that the alumina film does not exhibit a porous structure before reduction.

The coated nanowires are subsequently reduced with H2 (5% in Ar) at 650 °C for 1 h. It can be observed that the initial CuO nanowires, induced by the Rayleigh instability, undulate into separated nanoparticles (nanochains) confined in the nanotubes, as shown in Figure 1c,d.11 These nanoparticles in general have a short, rodlike shape and their diameters are controlled by the
inner diameters of the nanotubes. At this stage, it should be noted
that upon reduction the nanotube walls exhibit a porous structure
(Figure 1d) due to the removal (thermal decomposition) of the
interconnecting ethyl groups of the alucone films which is in
contrast to the compact Al2O3 films deposited with TMA and
H2O by atomic layer deposition (ALD). Recently, several
research groups reported on the production of porous films by
calcination or hydrolyzation of organic— inorganic hybrid poly-
mer films including alucone and zincone produced by MLD. Weimer et al. reported that an oxidation of alucone
films in air at 400 °C dominantly produced micropores with diameters of ~0.6 nm and a narrow size distribution as estimated by the
Horvath—Kawazoe method, in addition to some mesopores with diameters of ~3.8 nm as estimated by the Barrett—Joyner—
Halenda method. More mesopores formed at higher annealing
temperatures. Numerous mesopores with diameters of few
nanometers (below 5 nm) are indeed observed in the alucone
films after reduction as shown in Figure 1d. Thus, our results
comply with Weimer’s findings. From the experimental results
shown in this paper it can be assumed that channels are formed by
interconnection of the small pores to random and tortuous paths
throughout the coating. In addition, upon reduction the thickness of
the nanotube walls reduces from 37 to 25 nm (about 32% reduced),
pointing toward significant film shrinkage as a result of the removal
of the organic groups. This is similar to previous reports that showed
that the thickness of alucone films decreased by dehydration or
calcination in air at elevated temperatures.

Figure 2a,b shows the resulting samples after the above
embedded Cu nanoparticles were annealed in air at 400 °C for
1 h in a tube furnace. It can be observed that the embedded Cu
nanoparticles disappear. Instead, many smaller Cu oxide nano-
crystals form on the outer surfaces of the nanotubes. These
nanoparticles have a diameter below 80 nm and display a faceted shape (Figure 2b). TEM investigations do not reveal any obvious
structural transformation or broken areas of the nanotube walls,
indicating that the transformation of the inner Cu into outer Cu
oxide nanoparticles cannot be ascribed to large defects in the
nanotube walls such as holes. To investigate the crystalline status
and the phase of the oxide nanoparticles, high-resolution TEM
(HRTEM) investigations were conducted. Figure 2c shows
HRTEM images of two oxide nanoparticles. The interplanar
spacings 2.75, 2.33, and 1.88 Å match well with those for (110),
(111), and (−202) planes of monoclinic CuO, respectively. A
HRTEM image of a further oxide nanoparticle is displayed in
Figure 2d. The interplanar spacing of 2.45 Å corresponds with
that of (111) planes of primitive cubic Cu2O. On the basis of the
HRTEM investigations we can conclude that the attached
nanoparticles are highly crystalline CuO or Cu2O nanocrystals.

The crystallinity of the product was also confirmed by X-ray
diffraction (Figure S1 in Supporting Information). Previous
studies have demonstrated that an oxidation of copper in air
results in Cu2O as the main product, while CuO is formed slowly
through a further oxidation of Cu2O. In our study, nanocrystals
of both types (Cu2O and CuO) are produced by annealing
confirmed Cu nanoparticles in air, consistent with the previous
findings. Therefore, it can be speculated that Cu2O is initially
formed after diffusion of Cu to the nanotube surface and
subsequently some Cu2O nanoparticles are further oxidized to
form CuO. These Cu oxide nanoparticles could be further
reduced with H2 to produce supported metallic Cu nanoparticles
(Supporting Information Figures S2, S3).

The effect of the thickness of the porous Al2O3 films on the
morphology of the annealed products has been investigated in
detail. Figure 3a,b shows TEM images of the product obtained by annealing Cu nanoparticles embedded in porous
Al2O3 nanotubes with a wall thickness of 8 nm. The Cu nanoparti-
cles are dominantly transformed into large oxide particles
without a regular shape. They are randomly distributed on the
outer surfaces of the nanotubes. When the thickness of the films
is increased to 15 nm, Cu oxide nanoparticles with a smaller size
of about 20—80 nm and a faceted shape are produced as shown in
Figure 3c,d. A further increase in thickness to 50 nm shows
that Cu oxide nanoparticles with a similar morphology are still
produced despite the thick layer (Figure 3e,f). These nanoparti-
cles are smaller and show a more uniform size distribution and
also a faceted shape. These observations show that Cu
nanoparticles embedded in porous Al2O3 nanotubes can always
be oxidized to produce attached oxide nanoparticles and that
their size distribution becomes narrower with the increase of the
thickness of the porous shells.

To investigate the oxidation mechanism of the embedded Cu
nanoparticles, we performed a control experiment by annealing
Cu nanoparticles encapsulated in nonporous Al2O3 nanotubes,
which are prepared by reduction of CuO nanowires coated with
Al2O3 (15 nm) using TMA and water as precursors for an ALD
coating as described previously. The TEM images (Figure 4a—c)
show that each initial Cu particle is oxidized to a single Cu oxide
nanoparticle with a bent shape. The major part of the formed
nanostructures remains inside the nanotubes and some parts of
the nanostructures extrude from broken regions or crack lines
on the walls. This is in strong contrast to the Cu nanoparticles

Figure 1. (a,b) TEM images of CuO nanowires coated with a 37 nm thick alucone layer. (c,d) TEM images of Cu nanoparticles embedded in porous Al2O3 nanotubes obtained by reduction of the coated CuO nanowires in H2 at 650 °C.
Figure 2. (a,b) TEM images of Cu oxide nanoparticles supported on porous Al₂O₃ nanotubes produced by annealing Cu nanoparticles embedded in porous Al₂O₃ nanotubes (25 nm thick) at 400 °C in air. (c) HRTEM images of two oxide nanoparticles showing the {110}, {111}, and {−202} planes of monoclinic CuO. (d) HRTEM image of the boxed region of another oxide nanoparticle (inset) showing the {111} planes of cubic Cu₂O.

Figure 3. TEM images of Cu nanoparticles embedded in porous Al₂O₃ nanotubes with different wall thickness after annealing. (a,b) 8 nm; (c,d) 15 nm; (e,f) 50 nm.
encapsulated in porous Al₂O₃, which produce oxide nanoparticles attached to the outer surface. Since the oxidation of Cu nanoparticles occurred inside the nanotubes, it may be expected that the oxygen can diffuse inward through the nonporous Al₂O₃ shells. To verify this speculation, Cu nanoparticles confined in porous Al₂O₃ nanotubes (15 nm) and further coated with nonporous Al₂O₃ (15 nm) were annealed under the same conditions. Upon this procedure the inner Cu nanoparticles were not altered after annealing (Figure 4d,e), revealing that the outer nonporous Al₂O₃ coatings inhibit the oxidation of Cu. This result is in agreement with the report by Hakim et al. that showed that Fe nanoparticles coated with nonporous Al₂O₃ exhibit superior oxidation resistance. Therefore, the oxidation of Cu nanoparticles encapsulated in nonporous Al₂O₃ (Figure 4a–c) most probably origins from the exposed reaction of Cu with oxygen diffusing through broken regions and crack lines in the nanotube walls. The details will be discussed later.

Additional experiments were performed by annealing bare Cu nanoparticles, Cu nanoparticles coated with porous Al₂O₃, and Cu nanoparticles coated with nonporous Al₂O₃. For convenience, Cu nanoparticles supported on porous Al₂O₃ nanotubes (15 nm thick) produced by reduction of the Cu oxide nanocrystals as shown in Figure 3c,d were used for panels f–h. (i) By heating CuO nanowires coated with alucone (15 nm). All annealing experiments were performed in air at 400 °C for 1 h.
core by inward diffusion of oxygen gas, outward evaporation or/and diffusion of newly produced oxide, and recrystallization on the outer surfaces of the porous nanotubes). CuO nanowires coated with alumina (15 nm) were also heated in air at 400 °C for 1 h. Figure 4i shows the morphology of the alumina-coated CuO nanowires after annealing. Only some small voids are observed at the CuO/Al2O3 interface, indicative of a slight, extremely slow evaporation of CuO through the porous shell. Besides, there are no Cu oxide nanocrystals distributed on the outer surfaces of the nanotubes. This reveals that the outer oxide nanoparticles are not originating from the evaporation of/and diffusion of an inner Cu oxide intermediate. Thus, the three-step process mentioned above can be excluded.

On the basis of the above investigations, a schematic is displayed in Figure 5 to summarize the different oxidation behaviors of Cu nanoparticles under different surrounding environments by annealing in air. The formation of hollow Cu oxide nanospheres via the oxidation of uncoated Cu nanoparticles can be explained by the nanoscale Kirkendall effect.1–4,15–22 When Cu nanoparticles are exposed to air at elevated temperatures, an initial oxide layer is instantly formed on their surface due to the oxidation reaction. Because the outward diffusion of Cu ions in this oxide layer is much faster than the inward diffusion of oxygen, an inward flux of vacancies will lead to the formation of interior nanovoids at the CuO/oxide interface. With the inner Cu atoms gradually consumed following this unbalanced diffusion mode, the oxide layer will grow thicker and thicker. Finally, completely hollow Cu oxide nanospheres are formed. This evolution mechanism is illustrated in Figure 5a.

When the Cu nanoparticles are coated with a nonporous Al2O3 film (Figure 5b), the poor bulk solubility of both Cu and O2 in this amorphous structure makes the Al2O3 shell a superior diffusion barrier. Consequently, the contact between the inner Cu and the outer oxygen is blocked and the oxidation of Cu is prohibited even at high temperatures, as evidenced in Figure 4f. However, for the Cu/Al2O3 core—shell tubular nanostructures, thermal stress created at the Cu/Al2O3 interface during annealing can easily introduce failure of the coating, resulting, for example, in crack lines in the Al2O3 shell. Therefore, oxygen from the air can permeate the Al2O3 shell through those fractures and react with the inner Cu nanoparticles. It is reasonable to deduce that the subsequent oxidation still follows the nanoscale Kirkendall effect. The volume expansion caused by the generation of a hollow construction as well as the transformation of Cu to Cu oxide accounts for a partial extrusion of the oxides from broken regions or crack lines (Figure 4a–c). In this case the resistant role of the nonporous Al2O3 coating on the oxidation of Cu becomes invalid due to the leakage of oxygen from the air.

As we mentioned before, the porous Al2O3 film shows a different configuration feature compared with the nonporous film. The existence of abundant pores in the amorphous film provides many potential paths (nanochannels) connecting the inner core and the external environment. Figure 5c schematically shows the oxidation manner of Cu nanoparticles coated with such a porous film during annealing. In our case, the diffusion of both Cu at the Cu/Al2O3 interface and oxygen at the O2/Al2O3 interface is activated during the high-temperature annealing. The inner Cu cores tend to diffuse outward and outer oxygen inward along the nanochannels. However, the small size of the micropores, which is in the range of several angstroms on average, leads to a size selection for the diffusion rates of Cu and oxygen.14 Moreover, these pores are not straight, but tortuous, thus, the distance for a molecule to pass the film is largely exceeding the film thickness. The tortuosity of pores can also contribute to a size exclusion of various molecules because smaller molecules can more easily pass longer, more tortuous paths.23 Therefore, with a Cu atom being smaller than an oxygen molecule, the diffusive mass transfer of Cu outward through the nanochannels is more pronounced. The outward diffusing Cu will finally encounter oxygen at the pore opening, resulting in an oxidation of the copper. The continual outdiffusion of Cu and fusion/aggregation of neighboring Cu oxide clusters produce Cu oxide nanocrystals. The oxidation reaction will continue exploiting the net-outward diffusion of Cu until the whole Cu core is consumed. The directional outward growth mode finally leads to the formation of Cu oxide nanoparticles supported on the outer walls of hollow Al2O3 nanostructures. The diffusion of copper through the porous shell can be observed by mapping intermediate states of the nanostructures with energy-dispersive X-ray spectroscopy (EDX). For this purpose, the annealing process of Cu nanoparticles embedded in porous Al2O3 nanotubes was interrupted after 10 min. Figure 6a shows a typical scanning TEM (STEM) high-angle annular dark field image of the intermediate stage (also see Supporting Information Figure S4). Because of the incomplete diffusion process, both remaining nanoparticles inside the coating as well as oxide nanoparticles attached to the surface of the shell can be observed. EDX mapping revealed that Cu indeed is also present within the porous shell (Figure 6d). The Cu content was measured to be 1–3% by point analyses on various locations of the shell. These results clearly reveal the diffusion of copper through the porous Al2O3 shell and also the formation of copper oxide nanoparticles on the nanotube surface by comparing Figure 6b,d.
fractures in the nonporous Al$_2$O$_3$ film, as reflected in Figure 4a–c. When the Al$_2$O$_3$ film is porous, the existing nanopores in the Al$_2$O$_3$ can function as relaxation sinks for the Cu atoms under a high stress field. Once these Cu atoms diffuse into the nanopores, the outward mass transport of Cu becomes much faster because the diffusion along the pore walls can be greatly accelerated by the large curvature of the pores and a kinetically favorable surface diffusion process.\textsuperscript{24} According to this unique stress relaxation route as well as its high porosity, the porous Al$_2$O$_3$ coating behaves much more robust than the nonporous Al$_2$O$_3$ during annealing. On the basis of the above discussions, the dominant outward diffusion of Cu can be ascribed to both the small size of Cu atoms and the high thermal stress appearing at the Cu/Al$_2$O$_3$ interface.

A comparison of the two possible oxidation modes illustrated in Figure 5a–c shows that the oxidation front radiates from the Cu surface to the outer Al$_2$O$_3$ surface after the Cu nanoparticles are coated with a porous Al$_2$O$_3$ shell.\textsuperscript{17} The radial diffusion actually disassembles the continuous reactive Cu surface into discrete Cu clusters. As a result, the oxidation of Cu proceeds at multiple individual nucleation sites. It is reasonable to consider that the migration of initially formed Cu oxide clusters along the outer Al$_2$O$_3$ surface is restricted by the Al$_2$O$_3$ pore openings. Such a supportive traplike surface structure significantly reduces a particle aggregation, which results in a great dispersion of the oxides at the Al$_2$O$_3$ outer surface. This oxidation procedure represents a concerted disassembly and oxidation strategy, by which the fragmentation of a single Cu nanoparticle into a mass of supported Cu oxide nanoparticles is achieved. With a thicker porous Al$_2$O$_3$ coating and the resulting larger outer surface, assuming the density of pore openings at the porous Al$_2$O$_3$ outer surface is maintained constant, more pores with increased tortuosity are produced. This eventually leads to more, but smaller particles on the outer surface, since the volume of the initial Cu is largely equally distributed on the whole outer surface area, resulting in a better particle dispersion and size distribution of the supported Cu oxide nanoparticles, as shown in Figure 3.

In summary, we have demonstrated an unexpected oxidation mode of Cu nanoparticles embedded in porous Al$_2$O$_3$ films. The unique structure of the porous Al$_2$O$_3$ coating leads to the fragmentation of single Cu nanoparticles into many Cu oxide nanoparticles distributed on its outer surface during oxidation. The oxidation mechanism is explained by the dominating outward diffusion of Cu facilitated by the small size and tortuosity of the micropores in the films and the high thermal stress created at the Cu/Al$_2$O$_3$ interface. The subsequent reaction occurs at the pore openings, which work as multiple nucleation sites for the oxidation of the outward Cu flux. In addition, the thickness of the porous layer seems to provide a control over the size and number of the particles formed on the outer surfaces, which can be performed in a very precise way by MLD. Supported Cu nanoparticles are produced by the reduction of the oxide nanoparticles. The produced oxide and metal nanoparticles supported on Al$_2$O$_3$ nanotubes can find potential applications in many fields, like catalysis, sensorics, and so on.

ASSOCIATED CONTENT

Supporting Information. Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
E-mail: (Y.Q.) yqin@mpi-halle.de; (M.K.) mknez@mpi-halle.de.

ACKNOWLEDGMENT

This work was financially supported by the German Federal Ministry of Education and Research (BMBF) with the Contract Number FKZ: 03XS507.

REFERENCES


Figure 6. Elemental analyses of a porous nanotube (25 nm thick) with embedded Cu nanoparticles after partial diffusion by annealing in air at 400 °C for 10 min. (a) High-angle annular dark field STEM image. (b–d) Elemental maps of the boxed area in (a) for O, Al, and Cu, respectively. The scale bars correspond to 30 nm.

ASSOCIATED CONTENT

Supporting Information. Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
E-mail: (Y.Q.) yqin@mpi-halle.de; (M.K.) mknez@mpi-halle.de.

ACKNOWLEDGMENT

This work was financially supported by the German Federal Ministry of Education and Research (BMBF) with the Contract Number FKZ: 03XS507.

REFERENCES