Microelectronic Engineering 107 (2013) 229–232

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

# Synthesis of bimetallic nanoparticles in ionic liquids: Chemical routes vs physical vapor deposition

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ARTICLE INFO

*Article history:*
Available online 11 October 2012

*Keywords:*
Nanoparticles
Ionic Liquids
Chemical Synthesis
PVD

ABSTRACT

To meet the constant challenges of miniaturization in the microelectronics industry, new innovative pathways must be explored to produce nano-objects. Ionic liquids (ILs) can be used to generate and stabilize metallic nanoparticles (MNPs) by several physical and chemical routes. Here, the simultaneous decomposition of Ru and Cu organometallic precursors in IL is shown to yield core–shell Ru@CuNPs with smaller diameters and narrower size distributions than the corresponding monometallic NPs, in a broad range of Ru:Cu compositions. They are probably formed by rapid nucleation of Ru cores followed by decomposition of the Cu precursor on their surface. This effect forces the formation of a bimetallic structure that does not form with the use of purely physical processes such as PVD. These Cu, Ru, and Ru@CuNPs could be used for the formation of seed and barrier layers for the metallization of advanced interconnect structures.



## 1. Introduction

Recently, metallic nanoparticles have attracted much interest in a range of applications such as the fabrication of advanced microelectronic devices. For instance, they play a crucial role in the synthesis of nano-tubes or nanowires [1–3]. Also they can be used to replace continuous metallic layers to form more efficient and reliable devices [4]. Conversely, they could be precursors to build continuous and highly conformal metallic coatings [5,6]. For the metallization of through silicon vias in the 3D integration of interconnects, thin copper and ruthenium liners are of interest as seed- and barrier-layers respectively. Recently, alloyed copper layers have been investigated as so-called self-formed barriers [7]. In this view, it could be interesting to form bimetallic copper and ruthenium nanoparticles, which could be promising candidates for this application.

However; the controlled synthesis of metallic nanoparticles (NPs) in the range of 1–10 nm is still an on-going challenge, as is the understanding of their stabilization and agglomeration [8]. In particular, substantial effort has been centered on stabilizing transition-metal nanoparticles. Several strategies are known to stabilize metallic NPs, such as the use of polymers, ligands and organic or inorganic templates [9–11]. Unlike traditional solvents, ionic liquids (ILs) can be used to generate metallic NPs by several physical and chemical routes and stabilize them in the absence of further additives, inhibiting metal agglomeration to the bulk [12]. Ionic liquids are molten salts, generally liquid at room temperature, composed of an organic cation and an inorganic or organic anion. They are thermally and electrochemically stable, non-volatile and electrically conductive [13]. They exhibit a large degree of self-organization, enabling the generation of size-controlled metallic NPs by decomposition of organometallic precursors under dihydrogen ($H_2$), [14,15] or by evaporation or sputtering techniques [16]. In this article, we investigate the synthesis of Cu, Ru, and Ru–Cu nanoparticles in ionic liquids using both approaches.

## 2. Material and methods

### 2.1. Chemical synthesis of bimetallic nanoparticles

1-Butyl-3-methylimidazolium bistrifluoromethylsulphonylimide ($C_1C_4ImNTf_2$), IL, was synthesized from commercially available 1-methylimidazole, 1-butylchloride (Sigma Aldrich), and lithium bistrifluoromethylsulphonylimide (Solvionic) [17]. ($\eta^4$-1,5-Cyclooctadiene)($\eta^6$-1,3,5-cyclooctatriene)ruthenium(0), Ru(COD)(COT), was synthesized from $RuCl_3$–$3H_2O$, 1,5-cyclooctadiene, methanol

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0167-9317/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mee.2012.09.015

and zinc powder (Sigma Aldrich) [18]. Mesitylcopper(I), CuMes, (NanoMePS) was used without further purification.

After drying IL overnight at $10^{-8}$ bar, each organometallic precursor was dissolved separately under inert conditions and vigorous stirring to form a solution at $5 \times 10^{-2}$ M. The two mother solutions were mixed and stirred for 10 min in an autoclave under argon at room temperature, yielding a solution with the desired $M_1$:$M_2$ molar ratio.

The synthesis of the nanoparticles was conducted in a sealed reactor at 100 °C under pressure of $H_2$. In a first experiment, the mother solutions were used separately to evaluate reaction kinetics. Ru(COD)(COT) is fully decomposed within 30 min whereas CuMes needs several hours. Therefore all following experiments were carried out at 100 °C under 0.9 MPa $H_2$ for 4 h. The volatile products were quantified by gas chromatography in order to verify the stoichiometry of the reaction. For the experiment using $D_2$ instead of $H_2$, the released mesitylene was analyzed by exact mass spectrometry using a BrukermicroTOF-Q II Electron Spray Ionization Mass Spectrometer.

### 2.2. Chemical and PVD mixed synthesis of metallic nanoparticles

In a first step, RuNPs were synthesized using the chemical route described above. To form as small particles as possible, the synthesis was conducted at 0 °C, under 0.4 MPa $H_2$, during 72 h [15]. This procedure yields particles with a diameter of 1.4 ± 0.3 nm and concentration of 0.05 min solution, which was then diluted 10-fold.

In the second step, this suspension was loaded with copper (15 mg, giving an approximate 1:1 ratio) by evaporation from a 99.9995% pure copper target (www.smart-elements.com). For this purpose 40 ml of this Ru NPs/IL suspension was placed in the glass bulb of the reactor. During evaporation (approx. 30 min) the glass bulb was rotated at 5 rpm to form a homogenous film of the Ru NPs/IL suspension on the glass surface.

### 2.3. Characterization of bimetallic NPs

The NPs were observed by Transmission Electron Microscopy (TEM) using a Philips CM120 120 kV. For this purpose the suspensions of NPs in IL were deposited on a TEM grid and dried. For each sample, a least 100 NPs were measured. High Resolution Transmission Electron Microscopy (HRTEM) was performed on selected NPs in a Jeol JEM 2010 LaB6 working at 200 kV. Their chemical composition was assessed by Energy Dispersive X-ray (EDX) in the same equipment.

## 3. Results

### 3.1. Chemical synthesis of Ru–CuNPs

In a first approach monometallic NPs were formed by decomposition of the two Cu and Ru mother solutions as described above, affording CuNPs of 5.1[4.2;6.3] nm and RuNPs of 4.0[2.8;5.7] nm (Fig. 1).

Ru–Cu bimetallic NPs were tentatively synthesized from mixtures of the two mother solutions under the same conditions, according to Eq. (1):

$$\alpha\mathrm{Ru(COD)(COT)} + \beta\mathrm{CuMes} + x\mathrm{H_2} \rightarrow \mathrm{Ru_\alpha Cu_\beta} + 2\alpha\mathrm{COA} + \beta\mathrm{Mes\text{-}H} \quad (1)$$

which defines the molar fraction of Cu as $\chi_{Cu} = \beta/(\alpha + \beta)$.

The TEM picture corresponding to a 1:1 mixture ($\chi_{Cu} = 0.5$) is printed in Fig. 1. Remarkably, the size of the corresponding NPs is significantly smaller and less dispersed than that of the pure metals (diameter of 2.4 ± 0.5 nm vs. 4 and 5 nm diameters). Even more interestingly, this observation holds true for $\chi_{Cu}$ ranging from 0.005 to 0.91 [19]. HRTEM and EDX analyses show that the resulting NPs are composed of Ru and Cu, with a core of crystalline metallic hcpRu. Complementary analyses, such as Cu edge Electron Energy Loss Spectroscopy (EELS) and XPS indicate that Cu(0) forms a shell around the Ru(0) core [20]. The curve in Fig. 1 was computed assuming spherical Ru cores of 2 nm on which a Cu shell is built assuming a close-packed structure for this shell. When $\chi_{Cu}$ increases, the number of Ru cores in the Li decreases, and the quantity of Cu fixed on each individual NP increases, leading to larger NPs. Although simplistic, this model reasonably fits the experimental results [22].

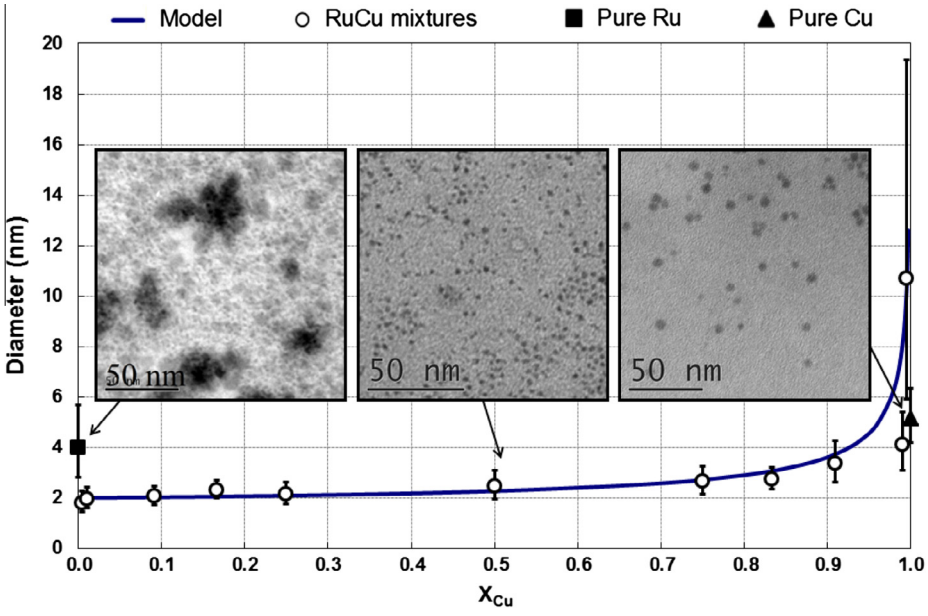


**Fig. 1.** Size evolution of Ru–Cu bimetallic NPs with initial composition of the solution. The size of Ru–Cu NPs (white circles) is plotted as a function of the molar fraction of Cu ($\chi_{Cu}$) in solution, and compared with pure Ru and pure Cu. Error bars correspond to ±2 standard deviations in the log-normal distribution. The solid line represents the size evolution expected from the formation of core–shell NPs with a 2 nm core of Ru and a shell of close-packed Cu. TEL images of $\chi_{Cu}$ values 0, 0.5, and 1 are also shown.