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Full Length Article

The influence of tertiary butyl hydrazine as a co-reactant on the atomic layer deposition of silver

Zahra Golrokhi[a], Paul A. Marshall[a], Simon Romani[a], Simon Rushworth[b], Paul R. Chalker[a], Richard J. Potter[a,*]

[a] Centre for Materials and Structures, School of Engineering,The University of Liverpool, Liverpool L69 3GH, UK
[b] EpiValence, The Wilton Centre, Redcar, Cleveland, TS10 4RF, UK

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ABSTRACT

Ultra-thin conformal silver films are the focus of development for applications such as anti-microbial surfaces, optical components and electronic devices. In this study, metallic silver films have been deposited using direct liquid injection thermal atomic layer deposition (ALD) using (hfac)Ag(1,5-COD) ((hexafluoroacetylacetonato)silver(I)(1,5-cyclooctadiene)) as the metal source and tertiary butyl hydrazine (TBH) as a co-reactant. The process provides a 23 °C wide 'self-limiting' ALD temperature window between 105 and 128 °C, which is significantly wider than is achievable using alcohol as a co-reactant. A mass deposition rate of ~20 ng/cm^2/cycle (~0.18 Å/cycle) is observed under self-limiting growth conditions. The resulting films are crystalline metallic silver with a near planar film-like morphology which are electrically conductive. By extending the temperature range of the ALD window by the use of TBH as a co-reactant, it is envisaged that the process will be exploitable in a range of new low temperature applications.

1. Introduction

Thermal atomic layer deposition (ALD) offers a highly desirable and perhaps even 'unique' combination of attributes that makes it highly attractive as a manufacturing process for applications where ultra-thin, conformal, pinhole-free coatings are required. Many of the desirable characteristics of ALD are directly related to the saturative surface reactions that are at the heart of 'self-limiting' ALD processes. The key advantages of ALD are, however, only realisable within a limited window of process parameters (temperatures, pressures, dose times, purge times etc) for each particular set of chemical reactants. In thermal ALD, temperature is a fundamentally important process parameter and the term 'ALD window' is widely used to define the range over which growth rate is independent of temperature. In terms of manufacturing, a wide 'ALD window' is advantageous as it means that larger spatial or temporal fluctuations in temperature can be tolerated, thus making the process intrinsically more stable, repeatable and easier to control. A reasonably wide ALD window is particularly important for coating large or complex three dimensional objects as uniform heating can be challenging.

The controlled deposition of ultra-thin conformal silver films is of great interest for applications such as anti-microbial surfaces [1], plasmonic enhanced thin film photovoltaics [2], highly reflective mirrors, catalysts [3] and gas sensors [4]. Relatively few studies on the ALD of metallic silver have been reported. Several have exploited plasma enhanced (PE) or radical enhanced (RE) ALD [5–8] and fewer have addressed thermal ALD [9–11] which is intrinsically more scaleable over larger areas. The plasma or radical enhanced ALD approach uses highly reactive co-reactant species which are generated from a plasma source, which offers both advantages and challenges in comparison to thermal ALD [12].

.One major advantage of PEALD (or REALD) is the use highly reactive species that are able to drive forward the surface reactions even at low temperatures, which means that they tend to extend the low temperature end of the ALD process window. For PEALD or REALD of silver, ALD windows of 20 °C has been reported [6], which is significantly wider than reported to-date for thermal ALD, where just one study has confirmed a 5 °C window [11]. On the flip side, one challenge associated with PEALD or REALD processes is that they rely on short-lived co-reactant species. The limited lifetime of these reactive species can become an issue if the process is to be used

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* Corresponding author.
E-mail address: rjpott@liverpool.ac.uk (R.J. Potter).

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to coat very large substrate areas or complex three-dimensional structures, particularly high aspect ratio ones.

The thermal ALD of ultrathin silver films has built on the earlier chemical vapour deposition (CVD) research, which has tended to focus on organofluoro complexes, amongst others. For example, Bahlawane et al. [13], demonstrated the growth of silver films by CVD using (hfac)Ag(1,5-COD) ((hexafluoroacetylacetonato)silver(I)(1,5-cyclooctadiene)) and various alcohols. The process exploits the catalytic reactivity of cationic silver, and the reactivity of alcohols with silver surfaces, whereby the affinity of cationic silver to alcohols and aldehydes leads to its chemical reduction. The same precursor has also been used to grow silver films in supercritical CO_2 using H_2 and acetone as the reducing agents [14]. However, the cyclic dosing of the precursor and co-reagent used in the ALD approach allows the influence of surface chemistry to dominate the growth mechanism. Liquid injection ALD was first used to demonstrate the growth of silver nanoparticles (NPs) [10] using the organometallic precursor (hfac)Ag(1,5-COD) dissolved in a 0.1 M toluene solution. The silver adsorbate species was reduced to metallic Ag NPs using intermittent pulses of propan-1-ol. Transmission electron microscopy reveals that the NPs deposited in the temperature range 110 °C–250 °C consist of face centred cubic, facetted silver crystallites. We have recently extended this work to establish the self-limiting growth regime for this process, hence enabling the deposition of ultra-thin conformal polycrystalline silver films [11]. Self-limiting growth was achieved within a narrow ALD temperature window between 123 and 128 °C which showed a mass deposition rate of ~17.5 ng per cm^2 per cycle. Pure metallic silver film with subsequent adsorption of atmospheric contaminants from air exposure was achieved in that study. The potential for exploiting other co-reactants for thermal ALD of silver, such as substituted hydrazine's (R_1HNNHR_2 where R_1 and R_2 represent alkyl substitution for example) was recognised by our group some time ago, leading to work that helped to support a patent application for SAFC Hitech [15].

The use of hydrazine based co-reactants in thermal ALD has not been widely reported to-date. A few studies report on the use of hydrazine based co-reactants as nitrogen sources for the deposition of metal nitrides [16–18]. To the best of our knowledge, only one experimental study by Knisley et al. [19] has previously reported on the use of hydrazine as a co-reactant for the ALD of a metal. Metallic copper was deposited using a three stage ALD process involving $Cu(dmap)_2$ ($dmap = OCHMeCH_2{-}NMe_2$), formic acid and un-substituted hydrazine. The formic acid is believed to form a copper formate, which is subsequently reduced to copper metal by the un-substituted hydrazine. The reaction scheme has been further elucidated by Dey and Elliot [20] via Density Functional Theory (DFT) modelling. The DFT study indicated that the formation of a formate intermediary is energetically viable during the first co-reactant dosing steps. The DFT study suggest that the hydrazine partially oxidises the formate, which then decomposes to CO_2 and in doing so reduces $Cu^{(+1)}$ to $Cu^{(0)}$. This DFT study indicates that co-reagents for metal ALD may not need to be limited to traditional reducing agents, but could also include reagent combinations that release electrons during oxidative decomposition [20]. Irrespective of the actual reaction mechanism in the Knisley study [19], they show that the un-substituted hydrazine on its own is not sufficient to form metallic copper from the $Cu(dmap)_2$ within the ALD temperature window.

In the current study, we looked at using a substituted hydrazine for the ALD of metallic silver. The choice of hydrazine derivative was based upon reaction chemistry to provide a single pathway to the target film while avoiding incorporation of unwanted elements. Un-substituted hydrazine (H_2NNH_2) in its anhydrous state is a toxic hazardous material that has explosive tendencies and so substitution to reduce risk is necessary for any process that is desired to be scaled safely to production volumes. The symmetric and unsymmetric dimethylhydrazines (MeHNNHMe, Me_2NNH_2) have been widely employed as alternatives however in the ALD process where surface reactions control the layer growth both compounds lead to the delivery of −Me groups to the surface that could lead to deleterious incorporation of carbon. To reduce the risk of such inclusions the tButyl substituted hydrazine ($tBuHNNH_2$) was chosen due to the beta hydride elimination pathway available to remove the tButyl group in a facile manner reducing potential C contamination [21]. In effect this enables the formation of H_2NNH_2 in situ at the surface which is sufficiently reactive to deposit metallic silver films.

The pKa value for TBH is 8.1 [22] whereas; the pKa for both propan-1-ol and butan-1-ol is 16.1 [23]. Therefore, alcohols are less acidic compared with hydrazines and so less favourable proton donors [24]. In this paper, a self-limiting thermal ALD process for the deposition of metallic silver thin films using TBH is presented and compared with the alcohol based silver ALD process previously presented [10,11]. To the best of our knowledge, this is the first ALD study that uses a substituted hydrazine as a co-reactant for the deposition of a metal. In this paper, we investigate the effect of using TBH as a reactive co-reagent for the thermal ALD of silver films. The purpose of this is to extend the "surface limiting" ALD process to lower temperatures and to examine the effect of this on the morphology of the silver films.

Table 1
ALD growth conditions.

Growth condition	Value			
Growth temperature	80–200 °C			
Reactor pressure	5 mbar			
Silver precursor	(hfac)(1,5-COD)Ag			
Silver source	0.1 M solution in n-Toluene			
Vaporizer temperature	130 °C			
Precursor delivery rate	17.5 µl/s			
Argon flow rate	200 sccm			
Co-reactant	Tertiary butyl hydrazine			
Co-reactant delivery	Vapour draw at ~20 °C			
ALD cycle	Inject	Purge	TBH	Purge
	0–6 s	4 s	0–4 s	0.5 or 4 s

2. Experimental procedure

2.1. ALD growth experiments

Films were deposited on as-supplied polished virgin test grade Si(100) (Compart Technology Ltd) and on soda-lime glass slides (Fisher Scientific) using a customised Aixtron AIX 200FE^{TM} reactor as described in reference [25]. A 0.1 M solution of (hfac)Ag(1,5-COD) (SAFC Hitech) in anhydrous toluene (Sigma Aldrich) was used as the silver source. This solution was introduced into the reactor by direct liquid injection via a Jipelec^{TM} vaporiser with a set-point temperature of 130 °C. The growth method and equipment used here replicates that used in our previous reported silver ALD study [11] except that the propan-1-ol was replaced with tertiary butyl hydrazine (TBH) (98%, HPLC grade supplied by SAFC Hitech Ltd) as the co-reactant. The TBH was introduced into the reactor via a Swagelok ALD valve using conventional vapour-draw sources held at room temperature (~20 °C). Further details of the growth conditions are described in reference [11] and are summarised in Table 1.

2.2. Physico-chemical characterisation

Film deposition rate was evaluated gravimetrically by measuring the mass change of 40 × 40 mm Si(100) samples after deposition