Surface chemistry of a Cu(I) beta-diketonate precursor and the atomic layer deposition of Cu₂O on SiO₂ studied by x-ray photoelectron spectroscopy

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(Received 29 January 2014; accepted 8 May 2014; published 21 May 2014)

The surface chemistry of the bis(tri-*n*-butylphosphane) copper(I) acetylacetonate, [(ⁿBu₃P)₂Cu(acac)] and the thermal atomic layer deposition (ALD) of Cu₂O using this Cu precursor as reactant and wet oxygen as coreactant on SiO₂ substrates are studied by *in-situ* x-ray photoelectron spectroscopy (XPS). The Cu precursor was evaporated and exposed to the substrates kept at temperatures between 22 °C and 300 °C. The measured phosphorus and carbon concentration on the substrates indicated that most of the [ⁿBu₃P] ligands were released either in the gas phase or during adsorption. No disproportionation was observed for the Cu precursor in the temperature range between 22 °C and 145 °C. However, disproportionation of the Cu precursor was observed at 200 °C, since C/Cu concentration ratio decreased and substantial amounts of metallic Cu were present on the substrate. The amount of metallic Cu increased, when the substrate was kept at 300 °C, indicating stronger disproportionation of the Cu precursor. Hence, the upper limit for the ALD of Cu₂O from this precursor lies in the temperature range between 145 °C and 200 °C, as the precursor must not alter its chemical and physical state after chemisorption on the substrate. Five hundred ALD cycles with the probed Cu precursor and wet O₂ as coreactant were carried out on SiO₂ at 145 °C. After ALD, *in-situ* XPS analysis confirmed the presence of Cu₂O on the substrate. *Ex-situ* spectroscopic ellipsometry indicated an average film thickness of 2.5 nm of Cu₂O deposited with a growth per cycle of 0.05 Å/cycle. Scanning electron microscopy and atomic force microscopy (AFM) investigations depicted a homogeneous, fine, and granular morphology of the Cu₂O ALD film on SiO₂. AFM investigations suggest that the deposited Cu₂O film is continuous on the SiO₂ substrate. © 2014 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4878815>]

I. INTRODUCTION

Cuprous oxide (Cu₂O) is a p-type semiconductor with a band gap of 2.3 eV.¹ It has widely attracted scientific and industrial interest for being an applicable material in many fields, such as large band gap material in solar cells,² high absorption material for sensors and photocells,^{3,4} batteries,⁵ catalysts,⁶ and channel material for the fabrication of thin film transistors.⁷

Recently, ultrathin films of Cu₂O are applied as the material to obtain copper (Cu) seed layers for electrochemical deposition (ECD) of metallic Cu in the ultralarge scale integrated electronic devices.^{8,9} The currently used physical vapor deposition processes for the deposition of the Cu seed layers, such as sputtering, are prone to nonconformal deposition within deep trenches.^{10,11} This may cause failure of interconnections due to formation of voids after Cu ECD, making applications in future technology nodes questionable. Hence, atomic layer deposition (ALD) is emerging as alternative method for the deposition of conformal and homogeneous ultrathin films on complex topographies and

large substrates in microelectronics. ALD is now also considered as a solution for conformal deposition of Cu seed layers on very high aspect ratio (AR) structures for technology nodes below 20 nm.^{11,12}

Cu seed layers have been deposited by direct ALD using metal organic precursor like copper(II) acetylacetonate, [Cu(acac)₂] (**1**) at temperatures below 150 °C.¹³ However, the necessity of H₂ plasma as reductant resulted in Cu films with a surface roughness around 2.5–3.0 nm for 25 nm thick films. This process could be problematic in high AR trenches and vias where ultrathin, conformal, and continuous Cu seed layers are required. Cu seed layer deposition by the reduction of Cu₂O, which was deposited by thermal ALD from bis(tri-*n*-butylphosphane) copper(I) acetylacetonate, [(ⁿBu₃P)₂Cu(acac)] (**2**), as Cu(I) β-diketonate precursor (Fig. 1) and wet O₂ as coreactant, was successfully carried out on different substrates such as SiO₂, Ta, TaN, and Ru.^{8,9,14} However, still many questions are unanswered regarding the underlying surface chemistry of this Cu precursor on many substrates, leading to different growth modes during ALD.¹⁴

In previous studies related to the chemical vapor deposition (CVD) of metallic Cu from Cu(I) β-diketonates, such as hexafluoroacetylacetonato Cu(I) vinyltrimethylsilane,

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[(TMVS)Cu(hfac)] (3), hexafluoroacetylacetonato Cu(I) 2-methyl-1-hexene-3-yne, [(MHY)Cu(hfac)] (4), hexafluoroacetylacetonato Cu(I) trimethylphosphine, [(hfa)CuPMe₃] (5), and (2-methyl-3,5-hexandionate) Cu(I) (bis(trimethylsilyl)acetylene), [(mhd)Cu(BTMSA)] (6), have depicted thermally induced disproportionation reactions producing Cu(0) and Cu(II) complexes as shown in Eq. (1).^{15–18} In these chemical reactions, the volatile Cu(II) byproducts, copper(II) hexafluoroacetylacetonate or Cu(II) (2-methyl-3,5-hexandionate), and the dissociated ligands (L), vinyltrimethylsilane or 2-methyl-1-hexene-3-yne or trimethylphosphine or (bis(trimethylsilyl)acetylene), are quite stable below 250 °C and leave the substrate without decomposition

With respect to the ALD from Cu(I) complexes, disproportionation destroys the self-limiting nature of the ALD process. Hence, for a successful ALD process any precursor molecule must not undergo any change in its oxidation state after chemisorption. Any change in the oxidation state is expected only during the second half-cycle of the ALD process. To date, very few knowledge on the initial chemisorption and surface reaction of the metal-organic Cu precursors is available with reference to the ALD of Cu and Cu oxides. Few investigations were carried out toward the understanding of the thermal chemistry of Cu precursors and the surface chemistry during initial half-cycle ALD reactions.^{19–21} Still, many issues are not clearly understood related to the initial surface chemistry of Cu precursors, such as lack of self-limited growth, stepwise conversion of ligands associated with the metal-organic precursors, and decomposition of the precursor in several steps generating different intermediates.^{22,23} Therefore, these individual surface phenomena must be properly understood for the systematic design of Cu ALD precursors and the improvement of the already existing ALD processes.

This paper presents the *in-situ* x-ray photoelectron spectroscopy (XPS) investigation of the surface chemistry of 2 during the ALD on SiO₂ substrate. The study reveals reporting vital information about the oxidation state and the atomic concentration after chemisorption on the substrates kept at different temperatures. The aim of the investigation is to understand the stepwise change in the precursor oxidation state with increasing substrate temperature and to identify the temperature limit for the thermal ALD with the mentioned Cu

FIG. 1. Molecular structure of the Cu(I) β -diketonate bis(tri-*n*-butylphosphane) copper(I) acetylacetonate, [(ⁿBu₃P)₂Cu(acac)] as metal organic Cu precursor for the ALD of Cu₂O.

precursor on SiO₂. In addition, *in-situ* and *ex-situ* investigations of ALD Cu₂O film are discussed as well.

II. EXPERIMENT

A. Substrate preparation

Si wafers of 200 mm received from Siltronic were cleaned in a NH₄OH:H₂O₂:H₂O (ratio 1:1:6) solution, followed by dipping in HCl:H₂O₂:H₂O (ratio 1:1:6) solution. SiO₂ of 20 nm were then grown by dry oxidation using HCl (3%) and O₂ at 900 °C. All wafers were then stored in ambient condition with no further treatment before the experiments.

B. Precursor dosing and ALD process

The initial half-cycle experiment was done by evaporating the Cu precursor onto the wafer. The wafer was then immediately transferred to the XPS chamber without vacuum break for investigation. The evaporation of the Cu precursor and the ALD processes were carried out inside the ALD chamber schematically shown in Fig. 2. The chamber is part of a 200 mm multi-chamber cluster deposition tool with a single wafer heater system. The ALD chamber is a vertical flow-type reactor pumped by a turbomolecular pump to a base pressure of 6.8×10^{-6} mbar. The process gases as well as the precursors are introduced into the reactor directly above the substrate heater. During the ALD processes, the reactor is pumped by a dry multi-stage roots pump achieving an average pressure of 1 mbar.

The liquid Cu precursor consisted of a mixture of 99 mol. % of 2 and 1 mol. % of (2,4-dimethylpentadienyl)(trimethylsilylcyclopentadienyl)ruthenium, [Ru(η^5 -C₅H₄SiMe₃)(η^5 -C₇H₁₁)] (7), as ruthenium precursor. The precursors were produced as reported in the literatures.^{24,25} As reported earlier, this precursor mixture is applied to produce Cu₂O films containing catalytic amounts of Ru, promoting the reduction of the copper oxide films towards metallic Cu by formic acid [HCOOH].^{26,27} When ALD of Cu₂O from this precursor mixture was carried out on SiO₂ and TaN substrates, remarkable improvement in

FIG. 2. Schematic diagram of the used ALD chamber, designed as a vertical flow-type reactor. The Cu precursor is evaporated in the Kemstream Vapbox direct liquid injection system and water is evaporated in the Brokhorst controlled evaporator and mixer unit. The respective vapor lines and the Ar purge gas line are connected to the reactor via control valves directly above the wafer.

the film chemistry was seen after subsequent reduction to metallic Cu also at low temperature of 115 °C with the vapor of [HCOOH].²⁸ In the XPS investigations after reduction of ALD copper oxide films, CuO species were completely transferred to the formation of metallic Cu on the sample. In addition, when the ALD Cu₂O film on SiO₂ from the pure precursor **2** was compared with the mixture of the **2** and **7**, no remarkable difference in the growth per cycle, film roughness, and morphology was observed.^{8,28} Hence, *in-situ* surface investigations are carried out only with respect to precursor **2** in the current study, because it was seen before that the ALD growth of the Cu₂O films was not affected by the addition of the catalytic amounts of precursor **7**.²⁸

The Cu precursor is thermally stable below 200 °C (Ref. 25) and stored in a stainless steel cylinder at room temperature. During the ALD processes, Cu precursor was evaporated by direct liquid injection using a Kemstream Vapbox 500 directly mounted on top of the reactor. The Vapbox mixes the Cu precursor with the Ar carrier gas and delivers the vapor into the ALD chamber through heated lines. Since the Cu precursor used for the experiments has a low vapor pressure (0.02 mbar at 98 °C),⁸ the Vapbox was heated to a temperature T_{vap} of 115 °C, in order to obtain sufficient vapor pressure and for preventing condensation inside the Vapbox. For the ALD process, water was evaporated in a Bronkhorst controlled evaporator and mixer liquid delivery system heated at 80 °C. During the precursor dosing steps and the purging steps of the ALD cycle, the water vapor was introduced into the bypass line.

For studying the influence of the evaporator temperature on the stability of the Cu precursor, T_{vap} was varied between 75 °C and 115 °C and the precursor was evaporated onto SiO₂ substrates kept at ambient temperature. The surface chemistry of the Cu precursor on SiO₂ was investigated at substrate temperatures T_{sub} between 22 °C and 300 °C. In the above mentioned processes, the ALD chamber was kept at 1 mbar average pressure and the Cu precursor vapor was dosed for 15 s. After exposure of the precursor onto the substrates, ALD chamber was pumped down to 2.5×10^{-2} mbar. The substrate was then transferred to the XPS chamber.

As reported earlier,¹⁴ for the ALD of Cu₂O using precursor **2** and wet oxygen as coreactant, 400 cycles were sufficient to obtain continuous growth of Cu₂O on SiO₂, so that the growth was then no longer substrate dependent and the surface roughness was independent on precursor dosing length above 3 s. Therefore, in the final experiment 500 cycles of Cu₂O ALD with the probed Cu precursor and wet oxygen as coreactant were carried out on SiO₂. The gas and liquid flow parameters are outlined in Table I. The precursor was evaporated at $T_{\text{vap}} = 115$ °C. Continuous argon purge gas was used while dosing the precursor and the coreactants. After each process, the wafers were immediately transported to XPS chamber for surface analysis.

C. *In-situ* XPS surface analysis

The surface chemistry of the Cu precursor and thin films of ALD Cu₂O were investigated in a PREVAC XPS system kept

TABLE I. Precursor and coreactants dosing lengths, and the respective liquid and gas flow schemes for the Cu₂O ALD on SiO₂.

Step	Process	Process liquid and gas	Flow rate	Dosing length(s)
1	Precursor dosing	Cu precursor Ar carrier gas	10 mg/min 1000 sccm	3
2	Purging	Ar	200 sccm	3
3	Coreactants dosing	Water vapor Ar carrier gas	25 mg/min 200 sccm	3
		O ₂	50 sccm	
4	Purging	Ar	200 sccm	3

at ultra high vacuum conditions of 1×10^{-9} mbar chamber pressure. The XPS system is mounted to the cluster tool, which was also used for the ALD, enabling XPS analysis without vacuum break. Monochromatic aluminum K α radiation (1486.6 eV) is provided by a VG Scienta MX 650 X-ray source and monochromator system. The energy distribution of the photoelectrons is measured by a VG Scienta EW3000 XPS/UPS/ARPES analyzer. This analyzer was operated at 200 eV pass energy. For analyzing the nonconductive samples, charge compensation using a low energy flood gun was carried out as follows: as suggested by Baer,²⁹ slight overcompensation of the surface charges was achieved by shifting the C1s peak position (284.6 eV)³⁰ to a lower binding energy (BE) position (281.0–283.0 eV). This was achieved by increasing the flood gun potential difference between 1 eV and 6 eV, keeping the flood gun current fixed at 250 μ A. Above 5 eV potential difference, the Cu 2p_{3/2} BE position had ‘locked’ with respect to the Si 2p_{3/2} BE position. Hence, the flood gun was operated at 6 eV potential differences and 250 μ A current in all the experiments. The BE scale was initially calibrated with a silver sample with the Ag 3d_{5/2} peak position at 368.5 eV. The measurement parameters and conditions were fixed throughout the experiments. Rescaling of the BE axis was carried out assuming no change in the substrate chemical state (Si 2p_{3/2} at 103.4 eV)³⁰ before and after the deposition of the ALD thin films. In addition, a Savitzky–Golay³¹ linear filtering algorithm with a smoothing width of 1 eV was applied to improve the signal-to-noise-ratio of the Auger spectrum. Casa XPS 2.3.16 Pre-rel 1.4 software was used for calculating the atomic concentration, rescaling of the BE axis, and smoothing along with the deconvolution of the Cu Auger spectra.

For the calculation of the atomic concentration in Casa XPS, Scofield relative sensitivity factors (RSFs) have been used.³² These RSFs were corrected for the monochromator-analyzer angle of 52.55°.³³ For the escape depth correction in Casa XPS a value of -0.75 was applied.³⁴ Oxidation states were identified using the absolute value of the Auger parameter (α). The Auger parameters were calculated by applying Eq. (2) alternatively written as Eq. (3), originally proposed by Wagner³⁵

$$\alpha = \text{BE} (i) + \text{KE} (jkl) - h\nu, \quad (2)$$

$$= \text{KE} (jkl) - \text{KE} (i). \quad (3)$$

TABLE II. Literature values of the Cu 2p_{3/2}, Cu L₃VV peak positions, and the Cu Auger parameter (α) of the Cu in different oxidation states and chemical phases.

Oxidation states	Cu in dispersed phase (Ref. 37)			Cu in thin films (Refs. 30 and 37)		
	Cu 2p _{3/2} (eV)	Cu L ₃ VV (eV)	α (eV)	Cu 2p _{3/2} (eV)	Cu L ₃ VV (eV)	α (eV)
Cu(0)	933.1	916.8	363.3	932.67	918.65	364.65
Cu(I)	932.8	913.6	359.8	932.4	916.8	362.6
Cu(II)	934.4	915.2	363.0	933.8	917.9	365.1

In Eqs. (2) and (3), BE (i) is the binding energy of an electron in orbital i , KE (jkl) is the kinetic energy KE (jkl) of the Auger transition jkl and KE (i) is the kinetic energy of the photoelectron emitted from the orbital i , and while $h\nu$ is the monochromatic x-ray excitation energy. The calculated values for α compared with the literature values are listed in Table II. According to Eq. (3), α is the difference between the KE of an Auger transition line and KE of a photoelectron line. Hence, it is independent of the reference level and static charging. Therefore, α can be directly taken as the chemical footprint of an atom in a certain oxidation state and chemical phase, equally valid for insulating substrates and metallic substrates.^{30,35} It must be noted that the Cu Auger KE (jkl) transition line consists of triplets, and the most intense transition line is termed as Cu L₃VV line,³⁶ which was considered as the Auger KE spectrum throughout the analysis. Since the Auger process in the transition metals from scandium to copper involves two valence electrons, the L₃VV Auger KE position in these elements is more sensitive to change in chemical environment compared to the photoelectron BE position.³⁶ In addition, it has also been observed that the Auger parameter α of Cu is sensitive to the amount of material deposited and the coordination number of an atom.^{37–40} However, α is also prone to higher measurement errors compared to the photoelectron BE position. As suggested in the literatures,^{29,41} errors in α were minimized by stabilizing the surface potential using a constant low energy flood gun potential difference and current for different experiments and recording the measurement after sufficiently long periods of x-ray exposure (10 min) to reach equilibrium.

D. Ex-situ analysis

Cu₂O film thickness and growth per cycle (GPC) were obtained by *ex-situ* spectroscopic ellipsometry (SE). SE of the Cu₂O film was carried out with SENTECH SE850 from Sentech Instruments GmbH supported by SpectraRay/3 analysis software. A Lorentz–Drude oscillator model⁴² was used to fit the measured Psi and Delta spectra in the spectral range between 380 nm and 830 nm. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) investigations of the same sample were also carried out to obtain information about the film morphology and surface roughness. The SEM investigation was carried out in a Carl Zeiss Supra 60 field-emission SEM system, operated with an acceleration voltage of 1 kV. A high efficiency in-lens secondary electron detector was used to collect the secondary electrons from the sample. The AFM investigation was carried out using a Veeco

Dimension 3000 operated in the tapping mode. A Si cantilever tip with a diameter less than 10 nm was used in the AFM.

III. RESULTS AND DISCUSSION

A. Surface chemistry of the Cu precursor

1. Influence of the evaporation temperature

SiO₂ is a very suitable substrate for the chemical investigation because XPS analysis depicted a carbon concentration less than 0.5% on the bare substrates. When the Cu precursor was evaporated in the Vapbox heated between 75 °C ≤ T_{vap} ≤ 115 °C onto SiO₂ kept at T_{sub} = 22 °C, *in-situ* XPS did not depict any change in the atomic concentration of the Cu precursor (Table III). The concentration ratios of phosphorus to copper ≈ 0.1 ± 0.01 and carbon to copper ≈ 6.0 ± 0.5, respectively, were identified at all investigated Vapbox temperatures. The low ratio of P/Cu suggests that the precursor releases its phosphine ligands during evaporation or upon chemisorption on the substrate. However, the Cu(acac) moiety appears to be stable, indicated by the C/Cu ratio of ≈ 6.0 ± 0.5, suggesting that the Vapbox temperature has no influence on the chemical state of the Cu precursor during the evaporation in this temperature range. Thus, T_{vap} = 115 °C was chosen as the fixed temperature for all further experiments, since it was sufficient to avoid condensation of the precursor in the Vapbox.

2. Influence of the substrate temperature

The *in-situ* XPS results of the Cu precursor evaporated on SiO₂ kept at 22 °C ≤ T_{sub} ≤ 300 °C is listed in Table IV and the respective C/Cu concentration ratio is plotted in Fig. 3. In the temperature range of 22 °C ≤ T_{sub} ≤ 100 °C, a ratio C/Cu ≈ 5.5 ± 0.4 and P/Cu ratio ≈ 0.1 ± 0.02 were observed. This again indicates that the precursor molecule lost most of the tri-*n*-butylphosphine [ⁿBu₃P] ligands after evaporation or

TABLE III. Atomic concentration of the Cu precursor on SiO₂ substrate kept at 22 °C, when the Cu precursor was evaporated between 75 °C and 115 °C.

S.N.	T _{vap} (°C)	Atomic concentration (%)					Ratio	
		Cu	C	P	Si	O	C/Cu	P/Cu
1	75	2.3	12.8	0.2	31.9	52.6	5.6	0.1
2	85	2.0	12.6	0.2	31.1	54.1	6.3	0.1
3	95	2.0	13.2	0.2	32.3	52.4	6.6	0.1
4	105	2.4	13.6	0.2	28.3	55.5	5.6	0.1
5	115	2.2	12.8	0.2	32.0	52.6	5.8	0.1

TABLE IV. Atomic concentration of the Cu precursor on SiO₂ substrate kept between 22 °C and 300 °C, when the Cu precursor was evaporated at 115 °C.

S.N.	T _{sub} (°C)	Atomic concentration (%)					Ratio	
		Cu	C	P	Si	O	C/Cu	P/Cu
1	22	2.2	12.8	0.2	32.0	52.6	5.8	0.1
2	55	1.97	12.3	0.2	32.3	53.3	6.1	0.1
3	75	2.4	12.6	0.2	32.2	52.8	5.3	0.1
4	100	2.3	13.6	0.1	31.7	52.4	5.9	0.04
5	145	2.3	12.2	0.1	32.4	53.1	5.2	0.03
6	200	2.7	10.1	0.1	32.3	54.8	3.8	0.03
7	300	4.5	10.2	0.1	31.2	54.1	2.3	0.02

upon chemisorption on the substrate. The comparison of the C/Cu and P/Cu atomic concentration ratio of the Cu precursor molecule, Cu precursor molecule without [ⁿBu₃P] ligands, and the Cu precursor after evaporation on SiO₂ kept at 145 °C are depicted in a bar diagram (Fig. 4). In the original Cu precursor molecule, the atomic concentration ratio of C/Cu = 29 and P/Cu = 2 are present. In contrast, Cu precursor after evaporation depicted C/Cu ≈ 5 and P/Cu ≈ 0. Actually, the identified atomic concentration ratio of C/Cu ≈ 5 is comparable to the original Cu precursor molecule without [ⁿBu₃P] ligands, i.e., [Cu(acac)] only. This indicates that most of the Cu precursor molecules on the substrate lose their phosphine ligands either during evaporation or immediately after chemisorption on the substrate.

At T_{sub} = 200 °C, C/Cu = 3.8 was observed, indicating thermally activated disproportionation and subsequent desorption of Cu(II) species from the surface. Furthermore, at

FIG. 3. Variation of C/Cu atomic concentration ratio of the Cu precursor evaporated on SiO₂ kept between 22 °C and 300 °C.

T_{sub} = 300 °C, C/Cu = 2.3 was observed, indicating even stronger disproportionation and desorption of Cu(II) from the surface. The results are consistent with the previous investigation of **5**, where this Cu(I) complex has disproportionated on SiO₂ at 300 °C, with desorption of copper(II) hexafluoroacetylacetonate and [PMe₃] leaving Cu(0) on the substrate surface.¹⁶

For identification of the oxidation state of the Cu precursor chemisorbed on the SiO₂ surface, the Auger parameter was calculated from the most intense Cu photoelectron peak and Cu Auger peaks. The peaks were identified by deconvoluting the experimentally obtained Cu 2p_{3/2} and Cu L₃VV spectra by Gaussian–Lorentzian mix spectra (GL30, 30% Lorentzian) as depicted in Figs. 5 and 6(a)–6(c). The oxidation state of Cu(0)

FIG. 4. Bar-diagram comparing the atomic concentrations of the original Cu precursor molecule, the Cu precursor molecule without the tri-*n*-butylphosphine ligands, and the Cu precursor molecule evaporated on SiO₂ kept at 145 °C.

FIG. 5. (Color online) Cu $2p_{3/2}$ spectrum of the Cu precursor evaporated on SiO₂ kept at 145 °C. Absolute values of the counts per second (CPS) are plotted against BE.

and Cu(I) states cannot be differentiated by the XPS core-level spectra of Cu $2p_{3/2}$ spectrum alone, since the binding energies of these states are superimposed.⁴³

Throughout the studied temperature range, the Cu $2p_{3/2}$ peak position was observed at 932.4 ± 0.1 eV as shown in Fig. 5, for $T_{\text{sub}} = 145$ °C, indicating the presence of Cu(I) or Cu(0) oxidation states and ruling out the presence of Cu(II) on the surface. In the temperature range of 22 °C $\leq T_{\text{sub}} \leq 100$ °C, Cu L_3VV , the Auger spectrum indicates only Cu(I) species on the

surface and an Auger parameter of 360.0 ± 0.2 eV was observed. This indicates the presence of precursor molecules, which have lost most of their [ⁿBu₃P] ligands. Similarly, as shown in Fig. 6(a), when the Cu precursor was evaporated on SiO₂ kept at $T_{\text{sub}} = 145$ °C, the Cu L_3VV Auger spectrum shows only Cu(I) species on the surface and Auger parameter of 359.8 eV is observed. This confirms the presence of precursor molecules without [ⁿBu₃P] ligands. Furthermore, in the Cu L_3VV spectrum at $T_{\text{sub}} \geq 200$ °C [Figs. 6(b) and 6(c)], the presence of substantial Cu(0) species in addition to Cu(I) species on the surface can be seen. Hence, this confirms that the Cu precursor has disproportionated on the surface, leading to the deposition of Cu(0), while the absence of Cu(II) species indicates complete desorption of Cu(II) compounds from the surface. The amount of Cu(0) [Fig. 6(d)] increased from 32.5% to 39.3% when the Cu precursor was evaporated on SiO₂ kept at $T_{\text{sub}} = 200$ °C and 300 °C respectively. This further confirms strong disproportionation of the Cu precursor leaving more metallic Cu(0) on the surface with increasing substrate temperatures above 200 °C. Hence, a substrate temperature between 145 °C and 200 °C was recognized as the upper limit for the thermal ALD of Cu₂O on SiO₂ for the probed Cu precursor.

Similar results were obtained in previous ALD experiments with this Cu(I) precursor on SiO₂ and TaN.⁸ A substrate temperature independent growth mode was observed between 110 °C and 125 °C on both SiO₂ and TaN substrates. Very smooth films on the SiO₂ substrate below 160 °C and below

FIG. 6. (Color online) Cu L_3VV Auger spectrum of the Cu precursor evaporated on SiO₂ at (a) 145 °C, (b) 200 °C, and (c) 300 °C. In (d), the amount of Cu(0)/Cu (%) is plotted against the substrate temperatures. Absolute values of the CPS are plotted against BE.

FIG. 7. (Color online) (a) *In-situ* XPS survey spectrum, (b) Cu 2p_{3/2}, and (c) Cu L₃VV Auger spectra of the Cu₂O ALD thin film deposited on SiO₂ at 145 °C. In the survey spectrum normalized counts per second (CPS) and in the targeted peak spectra absolute value of CPS are plotted against BE.

135 °C on TaN were obtained, since negligible CVD effects were present on the substrates at these temperatures.

B. ALD of Cu₂O at 145 °C

From the *in-situ* XPS investigations [Fig. 7(a)] after a complete ALD processes, a substantial amounts of Cu (Cu 2p = 18.6%) and oxygen (O 1s = 38.6%) were identified. However, the measured atomic concentration of oxygen was more than twice the one for Cu. Since, significant signal from the Si substrate (Si 2p = 17.0%) could also be seen, the measured oxygen concentration in the survey spectrum is a combined signal from the SiO₂ substrate and the film. The

Cu Auger parameter calculated from the deconvoluted Cu 2p_{3/2} and Cu L₃VV peaks as shown in Figs. 7(b) and 7(c) was found to be 361.8 eV, comparable to the Cu₂O in thin films (Table II). In addition, 10% of Cu complex, assumingly Cu(acac), was also identified in the Cu 2p_{3/2} spectrum [Fig. 7(b)], which could be from the unreacted Cu precursor molecule still present on the surface. P and C impurity contents of –P 2p = 1.8% and C 1s = 24.1% were also observed in the spectrum [Fig. 7(a)]. The presence of higher impurity contents after 500 complete ALD cycles could be due to either readsorption of released [¹⁸Bu₃P] ligands on the substrate or a

FIG. 8. Plan-view SEM image of the Cu₂O ALD thin film deposited on SiO₂ at 145 °C.

FIG. 9. (Color online) *Ex-situ* AFM investigation of the morphology of a Cu₂O ALD thin film deposited on SiO₂ at 145 °C. An RMS surface roughness of 0.24 nm was determined, similar to thermally grown SiO₂.

higher chemisorption probability of these ligands on Cu₂O compared to SiO₂ and incomplete conversion of [Cu(acac)] to Cu₂O during the oxidation pulses. However, this hypothesis requires comparative investigations using *in-situ* mass spectrometry. In a similar work for the ALD of metallic Cu from copper(I)-*N,N'*-di-sec-butylacetamidinate (**8**) and H₂ as coreactant on SiO₂, substantial carbon and nitrogen contaminations after the complete ALD cycles were observed.²⁰ The authors postulated that the contaminants could be due to readsorption of released butylacetamidinate ligands on the SiO₂ forming Si–O–C bonds and an incomplete removal of these ligands after hydrogenation.

From SE, an average film thickness of the ALD Cu₂O of 2.5 nm was found, resulting in a GPC of 0.05 Å/cycle. This value is comparable to previous experiments.^{8,9} The high resolution SEM image reveals a fine, granular, and homogeneous morphology of the Cu₂O film (Fig. 8). From the AFM investigations (Fig. 9), the root mean square surface roughness was found to be 0.24 nm, similar to that of the underlying SiO₂ substrate. This suggests that the Cu₂O film is closed resulting in a continuous thin film on SiO₂.

IV. CONCLUSIONS

In-situ investigation of the surface chemistry of the as Cu(I) β -diketonate precursor by *in-situ* x-ray photoelectron spectroscopy and the thermal ALD of Cu₂O from this precursor as reactant and wet O₂ as coreactant on SiO₂ were presented. Studying the surface chemistry of this Cu precursor on SiO₂ between 22 °C and 300 °C yielded vital information about its stability. Release of the [¹Bu₃P] ligands from the Cu precursor was observed in the investigated temperature range, either in the gas phase or immediately during the chemisorption process on the substrate. However, when evaporating the precursor at temperatures up to 115 °C, no negative influence on the stability of the Cu(acac) moiety during evaporation could be detected. Thermally induced disproportionation of this Cu precursor was observed only when the substrate was kept at 200 °C and above, with presence of substantial metallic Cu on the surface. At a substrate temperature of 300 °C, a stronger disproportionation reaction was observed, since the C/Cu ratio was reduced compared to room temperature and the percentage of metallic Cu increases substantially. Cu(II) species were not identified on the surface throughout the investigated temperature range. The results are consistent with the previous works on Cu(I) complexes. Hence, the upper temperature limit for the ALD of Cu₂O by the probed Cu precursor was found to be between 145 °C and 200 °C on SiO₂.

Five hundred ALD cycles on SiO₂ kept at 145 °C with the probed Cu precursor as reactant and wet O₂ as coreactant were then successfully carried out. *In-situ* XPS investigation revealed the presence of Cu₂O with carbon and phosphorous contaminants. Phosphorous and carbon concentration were 1.8% and 24.1%, respectively. Cu₂O of 2.5 nm was observed by the spectroscopic ellipsometry. This corresponds to a GPC of 0.05 Å/cycle, similar to previous experiments. SEM investigations show that very homogeneous, fine, and

granular coatings of Cu₂O on SiO₂ were formed. AFM investigations further suggested that the deposited Cu₂O film was continuous on the SiO₂ substrate.

For a deeper understanding, the *in-situ* XPS investigations will be combined with *in-situ* mass spectrometry in order to compare surface and gas phase chemical species of this Cu precursor after evaporation. Additional studies will be directed to the *in-situ* reduction of Cu₂O to metallic Cu.

ACKNOWLEDGMENT

This work was supported by the German Research Foundation (DFG) in the International Research Training Group (IRTG), Project GRK-1215 “Materials and Concepts for Advanced Interconnects and Nanosystems.”

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