Initial growth of chemical-vapor-deposited Ru from bis(hexafluoroacetylacetonate)dicarbonyl ruthenium

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Abstract

Deposition of ruthenium (Ru) was done using chemical vapor deposition with bis(hexafluoroacetylacetonate)dicarbonyl ruthenium ($Ru(hfac)_2(CO)_2$) as the precursor, at temperatures, T, ranging from $548 \leq T \leq 623$ K. The initial growth behavior on Si (100) surfaces was investigated using atomic force microscopy and X-ray photoelectron spectroscopy. Three-dimensional nucleus growth was observed. For $T=573$ K and a precursor partial pressure of 1.3×10^{-1} Pa, after 5 min deposition, the nuclei density observed on an H-terminated Si surface of 4.7×10^9 cm^{-2} was about three times that observed on an SiO$_2$ surface. Kinetic analysis of nucleation showed a lower activation energy on an H-terminated surface (5 kcal/mole) than that on an oxide surface (11 kcal/mol). As predicted by quantum chemical calculations, the much larger dissociation energy of Ru-hfac (241 kcal/mol) than of Ru–CO (57 kcal/mol) suggests that the deposition is mainly controlled by the hfac dissociation step. Moreover, the existence of adsorbed H was demonstrated to facilitate Ru deposition by removing hfac ligands through the formation of volatile H(hfac).
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1. Introduction

Ruthenium (Ru) has attracted much attention for use as an electrode material for high-dielectric capacitors that traditionally use tantalum oxide (Ta_2O_5), barium strontium titanate ($(Ba,Sr)TiO_3$), and lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) because Ru offers advantages of low resistivity, good dry etching ability, and superior chemical stability [1]. The oxide phase of ruthenium, RuO_2, a conductor with excellent chemical stability in high-temperature O_2 atmospheres, is promising for use as diffusion barriers for contact metallizations in very large scale integration components and as electrodes for PZT-based ferroelectric random access memory applications [2–4].

For fabricating Ru-containing thin films, chemical vapor deposition (CVD) has attracted the most attention because it permits deposition of conformal films on uneven surfaces and selective growth, neither of which can be achieved by the use of physical vapor deposition techniques. Several metallorganic compounds have been proposed as CVD-Ru source reagents. They include (i) ruthenocene [5] and its alkyl substituted derivatives such as bis(ethylcyclopentadienyl) ruthenium ($Ru(C_5H_4Et)_2$) [6], (ii) metal carbonyl complexes such as ruthenium carbonyl ($Ru_3(CO)_{12}$) [7] and tetracarbonylhexafluoro-2-butyene ruthenium ($Ru(CO)_4(hfb)$) [8], and (iii) tri-β-diketonate coordination complexes such as tri(acetylacetonate) ruthenium ($Ru(acac)_3$) [9]. Among these precursors, $Ru(C_5H_4Et)_2$ is attractive, because it is a liquid at STP and is easily vaporized. However, its main disadvantage is its poor decomposition characteristics, which result in long incubation times for film growth [10,11].

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To meet the demand for a better Ru-CVD process, a new Ru precursor called bis(hexafluoroacetylacetonate)-dicarbonyl ruthenium ($Ru(hfac)_2(CO)_2$) has been developed by us, which has two *cis*-oriented CO ligands and a pair of chelating β-diketonate ligands with CF_3 substituents [12–14]. A basic study about the growth behavior of $Ru(hfac)_2(CO)_2$ showed that this precursor may yield superior crystallinity and step coverage compared to that achieved with most volatile carbonyl complexes, i.e., $Ru(CO)_5$ and $Ru(CO)_4(hfb)$, and to those of the commercially available liquid ruthenocene reagent $Ru(C_5H_4Et)_2$. However, the film-growth mechanism of $Ru(hfac)_2(CO)_2$, especially its surface-reaction kinetics, remains unclear.

Here, we present a study of the initial nucleation of Ru from $Ru(hfac)_2(CO)_2$ on Si substrates with various surface termination species. By using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to do kinetic analysis of the first stage of Ru nucleation, a surface-reaction mechanism was proposed. Moreover, using molecular orbital calculations, theoretical analysis of the fundamental molecular structure of the precursor was made to assist with the construction of the surface chemistry mechanism.

2. Experimental details

A cold-wall CVD reactor (detailed description is available elsewhere [15]) was used for film deposition. The apparatus consisted of a precursor feed line, a reaction chamber, and a pumping system. The precursor used was bis(hexafluoroacetylacetonate)dicarbonyl ruthenium ($Ru(hfac)_2(CO)_2$), which was contained in a vaporizer with its temperature regulated by a thermal bath. Either nitrogen (N_2, 99.999%) or hydrogen (H_2, 99.999%) was passed through the vaporizer to carry the precursor vapor to the CVD reactor. The precursor stream was then combined with either the dilute N_2 or H_2 stream before introducing it into the reactor. The total pressure, P, was kept constant at $P=67$ Pa.

We used P-type Si (100) substrates with 10 Ω cm resistivity. The wafers were cleaned by using standard wet chemical procedures as follows. First, the wafers were cleaned using methanol and acetone, in turn, in an ultrasonic bath. Then, the so-called SC-1 and SC-2 procedures were used to remove surface contaminants and to form a uniform oxide layer [16–18]. After these treatments, the wafers were rinsed in deionized water and dried by using a jet of filtered N_2. The wafers thus prepared had a layer of OH groups on the surface and therefore were hydrophilic, as can be checked by a complete wetting when they were immersed in deionized water and pulled up again. To obtain H-terminated surfaces, a sample was etched back in an HF solution (1.0 wt.%) for several seconds until it became completely hydrophobic. Afterwards it was rinsed in

deionized water for approximately 15 s and dried by using a jet of filtered N_2. The surface-treated sample was immediately mounted on a stainless-steel substrate holder in the reactor and prepared for deposition. The holder was heated by an IR lamp. The temperature of the holder was regulated through a proportional integral derivative controller with a thermo-couple embedded just beneath the holder. For deposition on a biased substrate, a direct current (dc) voltage was applied to the stainless-steel substrate holder, which was electrically isolated from the reactor chamber. The applied dc bias voltages varied from −5 to 5 V. Table 1 lists the experimental conditions used in this work.

Because the OH-termination on Si with an ultra-thin oxide layer converts to an O-terminated surface for $T>448$ K [19], deposition done on OH-terminated surfaces in the temperature range $548 \leq T \leq 623$ K should be considered as deposition on O-terminated SiO_2 surfaces, which is referred to as an "O-terminated surface" in this work.

After deposition, the morphology of the substrate surface was observed by an AFM (Digital Instrument, Nano-scope III). The AFM observation was performed under a tapping mode using a Si cantilever with force constant of 28–48 N/m. A typical scan range of the piezoelectric scanner was 2×2 μm^2 using a scan rate of about 0.5 Hz with 512 number of samples. The chemical composition of the deposits was investigated by using X-ray photoelectron spectroscopy (Thermo VG, Theta Probe) with an Al K_α (1486.6 eV) X-ray source. To obtain reliable peak shapes, each peak was scanned 40 times with a scan step of 0.05 eV and with a pass energy of 50 eV. Because the XPS peak intensity ratio of Ru $3d_{5/2}$ to Ru $3d_{3/2}$ for Ru metal is a constant (1.5), a curve fitting program was used to separate the overlapping curves between C 1s (284.6 eV) and Ru $3d_{3/2}$ (284.0 eV) by maintaining the Ru $3d_{5/2}$ to Ru $3d_{3/2}$ peak intensity ratio as a constant of 1.5 using a Gaussian–Lorentzian line shape and Shirley baseline [14]. Moreover, to explore the different interactions between the precursor and the surface terminations, all ab initio calculations were done with the GAUSSIAN 98 program [20]. The geometry optimization and vibrational frequencies of the $Ru(hfac)_2(CO)_2$ and its fragments were calculated by using the Becke3-LYP level with the STO-3G. basis set. The minima (number of imaginary frequencies) were confirmed through the calculations of harmonic vibrational frequen-

Table 1
Deposition conditions for the initial growth of Ru

Precursor	$T_{bubbler}$	$P_{bubbler}$	Carrier gas flow rate
$Ru(hfac)_2(CO)_2$	313 K	4.8×10^4 Pa	4 sccm

Total flow rate: 25 sccm (N_2 or H_2 diluted); total pressure: 5 torr; substrate temperature: 548–623 K; substrate bias: −5–5 V.