Low-Temperature Chemical Vapor Deposition of Ruthenium Dioxide from Ruthenium Tetroxide: A Simple Approach to High-Purity RuO_2 Films

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Introduction

Films of ruthenium dioxide are important for several electronic[1] and electrochemical[2] applications, and are usually obtained by solution methods from ruthenium(III) chloride or other ruthenium compounds. Such films of RuO_2 are often contaminated with chloride impurities and show poor adhesion.[1,2] Recently, the preparation of high-quality RuO_2 thin films on silicon wafers has become of interest for electrode structures for developing new ferroelectric memories based on lead zirconate titanate (PZT).[3] Deposition of PZT films by a sol–gel process has been well established,[4] but since uniform, adherent RuO_2 films are difficult to prepare using such solution methods, the synthesis of RuO_2 films by chemical vapor deposition (CVD) is attractive. Pure ruthenium films have been prepared by CVD from several precursors, such as $[Ru(acac)_3]$, acac = acetylacetonate or its fluorinated derivatives,[5–7] $[Ru_3(CO)_{12}]$,[5] $[Ru(C_5H_5)_2]$,[5,8] and $[Ru(CO)_4(CF_3C{\equiv}CCF_3)]$.[9] CVD of RuO_2 has been achieved previously from $[Ru(C_5H_5)_2]$ or $[Ru(acac)_3]$ in the presence of oxygen, but the films contain carbon impurities.[5–8] Nevertheless, the RuO_2 films prepared from $[Ru(C_5H_5)_2]$ or $[Ru(acac)_3]$ in the presence of O_2 at 575 °C showed resistivities $\rho = (8.99\text{–}64.3) \times 10^{-5}\ \Omega$ cm, which may be compared to that of RuO_2 single crystals [$\rho = (3.5\text{–}5) \times 10^{-5}\ \Omega$ cm] and superior to those prepared from pyrolysis of ruthenium salts.[2a] CVD in the presence of hydrogen can often reduce carbon contamination, but this method cannot be used in this case since CVD from metallorganic ruthenium precursors in the presence of hydrogen gives ruthenium metal and not RuO_2.[5–9] Clearly, for CVD of pure RuO_2, a precursor which does not contain either carbon or halogen is desirable. This article reports that RuO_4 is an excellent precursor for CVD of RuO_2 and, since the only other product is O_2 (eq 1), the films are of high

$$RuO_4 \rightarrow RuO_2 + O_2 \quad (1)$$

purity. It has previously been noted that thermal annealing of RuO_2 films can lead to loss of ruthenium by disproportionation to Ru + RuO_4, which is volatile, and that vapor transport and crystal growth of RuO_2 at 1100 °C may involve the reversible formation of volatile RuO_4.[5,10] The boiling point of RuO_4 is 129 °C (it melts at 27 °C), so it is much more volatile than metallorganic precursors.[10–14]

RuO_4 **[caution]**[15] is obtained by oxidation of ruthenium salts under basic conditions[10] and is commercially available in aqueous solution (Strem Chemicals). Solutions of RuO_4 in CCl_4 or pentane, which have limited thermal stability, were easily obtained by solvent extraction and pure RuO_4 was obtained from the pentane solution by removing the solvent under vacuum (10^{-3} Torr, ca. –60 °C). Using solutions of RuO_4, CVD was carried out in a vertical cold-wall reactor at atmospheric pressure with a substrate temperature of 150–220 °C, using a carrier gas of air or nitrogen for the solutions in CCl_4 or pentane (Table I), while CVD from pure RuO_4 was performed using a horizontal hot-wall reactor at 150 °C at atmospheric pressure with no carrier gas (Table II).

CVD using aqueous RuO_4 with the substrate at 150 °C gave pure RuO_2, but the film morphology was very rough and there were many fracture lines. From pentane solutions of RuO_4, the film morphology was smooth, but adhesion to glass or silicon substrates was poor. The vapor

Table I. Deposition Conditions and Film Properties of RuO_2 from RuO_4 Solutions

solvent for RuO_4	pressure carrier gas	substrate temp, °C	substrate	film morphology and color	adhesion	XPS analysis[a]		
						Ru	O	Cl
water	1 atm	150	glass	rough black	fair	18.7	81.3	
water	10^{-1} Torr	180	glass	rough black	poor	26.5	72.3	1.2[b]
water	1 atm	200	glass	rough black	poor	21.3	72.9	5.8[b]
water	1 atm	150	Si(100)	rough black	fair	21.1	78.9	
CCl_4	1 atm/air	220	glass	shiny blue-black	good	25.8	64.7	9.5
CCl_4	1 atm/air	220	Si(100)	shiny blue-black	good	21.3	72.9	7.8
pentane	1 atm/air	150	glass	shiny black	poor	30.2	69.8	

[a] Calculated values for RuO_2 are Ru, 33.3; O, 66.7. Values are given in atom percent. [b] Chlorine arises in nonreproducible amounts from impurities in commercial aqueous RuO_4. No carbon was detected in any of the samples.

Table II. Atmospheric Pressure CVD of RuO_2 from RuO_4

substrate	substrate temp, °C	film appearance	adhesion	XPS analysis[a]	
				Ru	O
glass	150	shiny dark-blue	excellent	26.4	73.6
Si(100)	150	shiny purple	good	24.0	76.0
Al	150	shiny purple	excellent	25.0	75.0

[a] Analysis in atom percent. Theoretical values are Ru, 33.3; O, 66.7%.

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(15) RuO_4 is volatile and toxic. It must be handled in a well-ventilated fumehood. Pure RuO_4 has been reported to explode when heated above 100 °C,[10,11] and it may react violently with organic substances.

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Figure 1. SEM images of films of RuO_2 prepared by atmospheric pressure CVD from RuO_4: (a) Using aqueous RuO_4 with glass substrate at 150 °C. (b) Using RuO_4 in CCl_4 solution on glass substrate at 220 °C. (c) Using pure RuO_4 on Si(100) substrate at 150 °C. (d) As for (c); cross-section view.

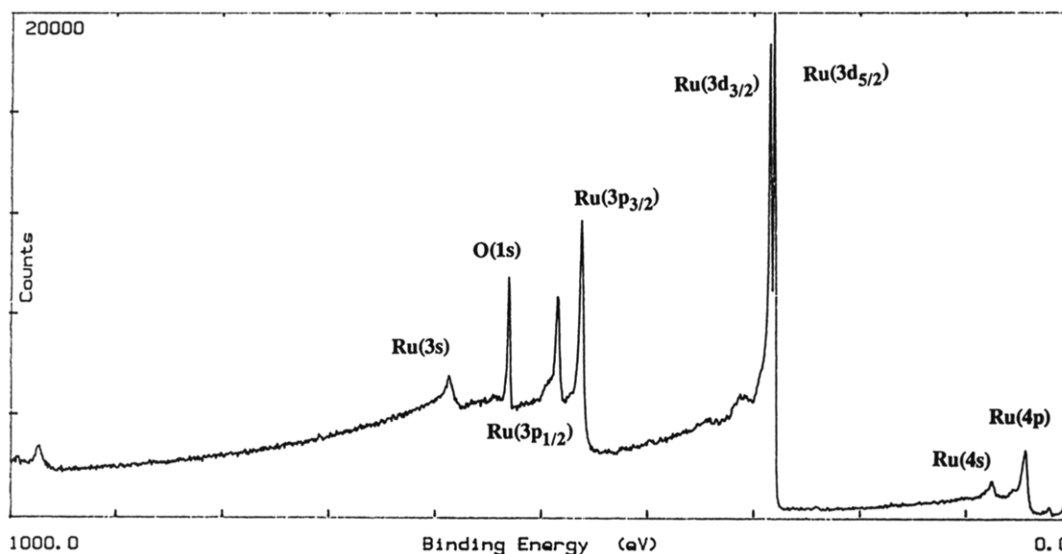

Figure 2. Typical XPS spectrum of a RuO_2 film grown from pure RuO_4 on Si(100).

transport of RuO_4 from CCl_4 solution at room temperature and atmospheric pressure was found to be much slower than from aqueous solution but, using a carrier gas of air or nitrogen, films could be grown with the substrate heated to 220 °C. Low-pressure CVD was less satisfactory since much of the RuO_4 failed to decompose even with the substrate at 250 °C. The film morphology and adhesion were both excellent in the films grown from CCl_4 solution but the films contained significant impurities of chloride (Table I). Using pure RuO_4 as precursor, films were grown

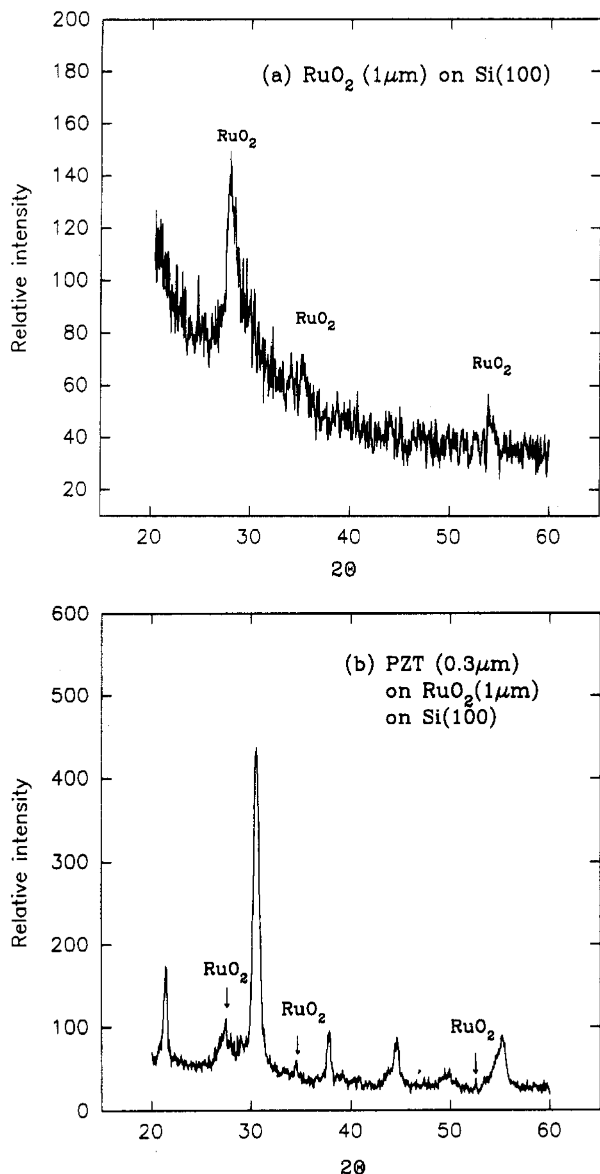

Figure 3. X-ray diffraction patterns: (a) for RuO_2 film on Si(100); (b) for a lead zirconate titanate (Zr/Ti = 40/60) ferroelectric film deposited on a RuO_2 film. RuO_2 peaks are noted.

most easily using a horizontal hot-wall CVD reactor at atmospheric pressure with the substrate at 150 °C. Under these conditions, the film morphology, adhesion and purity were all excellent (Table II). In a typical experiment, a film of 1-μm thickness was deposited on a silicon wafer in 2 h with the precursor at room temperature. Since the volatility of the precursor is high, the deposition rate could be greatly increased, and a 1-μm film could be grown in a few minutes by using a partial vacuum or by warming the precursor reservoir.

The film morphologies were studied by SEM and typical images are shown in Figure 1. Films prepared from aqueous RuO_4 were dull black in color and SEM analysis indicated that the films were cracked and inhomogeneous (Figure 1a). However, films prepared from CCl_4 solution appeared as shiny dark blue mirrors and SEM analysis confirmed their smooth, homogeneous nature (Figure 1b). Similarly, films prepared from pure RuO_4 were of high quality (Figure 1c,d); they adhered well to all of the substrates tested and a film on glass was not etched by acid or base. The XPS spectra of all films showed the Ru ($3d_{5/2}$) peak at 280.6 eV in good agreement with authentic RuO_2 (Figure 2). The oxygen (1s) chemical shift was 530.1 eV, and for CVD from pure RuO_4, the Ru:O ratio was typical of bulk RuO_2 (Tables I and II; note that oxygen analyses are always slightly higher than the theoretical values due to surface effects). However, for CVD from aqueous RuO_4, the RuO_2 film obtained at 150 °C gave a Ru/O ratio much lower than the expected value of 1:2. It is likely that the RuO_2 film is hydrated, perhaps $RuO_2{\cdot}H_2O$ which is a black solid obtained previously by reaction of RuO_4 with H_2, and which undergoes dehydration only at 587 °C.[10] The XPS spectra of films of RuO_2 obtained from aqueous RuO_4 contained an additional, partially resolved band due to O(1s) at 531–532 eV, which may be due to water in the RuO_2.

The electrical conductivity of the RuO_2 films was measured using gold electrodes evaporated on the face of the sample. The resistivity of a film of thickness approximately 1 μm is approximately 10^{-2} Ω cm.

To assess the application of CVD RuO_2 films for ferroelectric device purposes, lead zirconate titanate films 0.3 μm thick were prepared on a 1-μm-thick RuO_2 layer using a sol–gel technique.[4] The sample was fired in air on a hot plate at 400 °C for 10 min and then annealed to a fully crystallized state by rapid thermal processing in an AG Associates HeatPulse 410 Rapid Thermal Processor for 30 s at 650 °C. The resulting films were crack-free and had crystallized readily to the perovskite phase (Figure 3). The figure also shows the characteristic diffraction peaks of RuO_2. After evaporating gold upper electrodes, a ferroelectric hysteresis loop was achieved using standard methods[16] with a remanent polarization of 30 μC cm^{-2} and a coercive field of 150 kV cm^{-1}. While these values are not yet optimized, this performance indicates that RuO_2 prepared by CVD has promise as a substrate for ferroelectric thin films. This is likely due both to the ability of RuO_2 to sustain its conductivity during PZT processing and to enhance the nucleation of the perovskite phase in PZT.

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