Available online at www.sciencedirect.com
SCIENCE DIRECT
Materials Chemistry and Physics 93 (2005) 142–148
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Metallorganic chemical vapor deposition of metallic Ru thin films on biaxially textured Ni substrates using a $Ru(EtCp)_2$ precursor

Hu-Yong Tian [a,b,*], Helen-Lai-Wa Chan [a], Chung-Loong Choy [a], Jong-Wan Choi [b], Kwang-Soo No [b]

[a] *Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*
[b] *Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-Gu, Daejeon 305-701, South Korea*

Received 7 July 2004; accepted 6 March 2005

Abstract

Ruthenium (Ru) films on rolling-assisted biaxially textured Ni substrates (RABiTs) were deposited by liquid source chemical vapor deposition using bis-(ethyl-π-cyclopentadienyl)ruthenium ($Ru(C_2H_5C_5H_4)_2$). The thermal decomposition process of the precursor was investigated by Fourier transform infrared spectroscopy (FTIR), mass spectroscopy, and differential scanning calorimetry/thermogravimetric analyses (DSC/TGA). The crystalline structure and resistivity of Ru thin films were investigated. The Ru films were polycrystalline and had a grainy structure. Although the thermal decomposition of the precursor required a sufficient amount of oxygen, the experimental results showed that up to a certain concentration of oxygen (i.e. $O_2/Ar \sim 30/10$), Ru metal film was deposited without any detectable RuO_2 impurities. A higher deposition temperature and a higher ratio of O_2/Ar will be beneficial to the growth of (0 0 2) orientation. They showed a low resistivity of about 10–20 μΩ cm, which is sufficiently low for them to be used as a buffer layer in superconductor tapes or electrode materials in dielectric capacitors.

Keywords: Metal films; Chemical vapor deposition; Auger spectrum; Resistivity

1. Introduction

Ruthenium is one of the most promising candidate electrode materials for some dielectric capacitors [1–3]. Ru and RuO_2 thin films have been receiving much attention because of their good conductivity, low temperature coefficient of resistance (TCR), and high thermal stability [4]. Therefore, they have been investigated for many applications such as diffusion barriers for oxygen [5,6], thin film resistors, and electrode materials for ferroelectric oxides [7,8]. Recently, there has been increasing interest in the deposition of metallic Ru films as well as in the study of RuO_2 film because Ru film can be used as an adhesion layer for a diffusion barrier as well as an electrode for dynamic random access memory (DRAM). Metallic Ru films on Si and SiO_2/Si substrates were prepared by metallorganic chemical vapor deposition (CVD) using a new precursor named (η^6-benzene)(η^4-1,3-cyclohexadiene)ruthenium ($Ru(C_6H_6)(C_6H_8)$) in Ar atmosphere. The Ru films contained hydrogen that originated in the hydrogen atoms in the precursor and was involved in the CVD process due to the catalytic effect of ruthenium on hydrocarbon and hydrogen [9]. The thermal decomposition of the precursor, bis-(ethyl-π-cyclopentadienyl)ruthenium ($Ru(C_2H_5C_5H_4)_2$), required a sufficient amount of oxygen up to a certain concentration of oxygen. Ru films were deposited without any detectable RuO_2 impurities [10]. The key issue of the liquid delivery technique depends on the stable vaporization of the source in the vaporizer. In order to solve problems such as decomposition and the instability of the supply, the precursor was dissolved into tetrahydrofuran (C_4H_8, THF) solvent [11].

* Corresponding author. Tel.: +852 27764616; fax: +852 23337629.
E-mail address: tianhuyong@hotmail.com (H.-Y. Tian).

0254-0584/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2005.03.002

Recently, many studies have demonstrated that sharply biaxially textured nickel could be produced in long lengths by thermo-mechanical processing techniques [12–14]. To date, some researchers have focused their investigations on proper buffer layers, as it is well known that proper buffer layers are critical to formation of epitaxially oxide buffer layers on the rolling-assisted biaxially textured Ni substrates (RABiTs) surface that are mechanically robust and chemically inert with respect to both the substrate and the high temperature superconductor (HTS) films.

It is important to utilize any of these buffer layers deposition techniques to prevent unfavorably oriented NiO on the Ni surface. Ru or RuO_2 thin films as an electrode material, as mentioned above, have drawn attention because of their good conductivity as well as excellent barrier properties against oxygen diffusion [5,6,15]. However, few studies about pure metal ruthenium deposition have been reported so far, because the precursors involve oxygen atom or oxygen gas as a reaction to assist the deposition of the precursor. The purpose of the present work is to obtain information about the mechanism of the thermal decomposition of the precursor and to determine the optimum conditions for obtaining pure metal Ru films without NiO formation by oxidizing the substrate in the presence of oxygen. In this work, we investigated the microstucture and relationship between processing conditions and properties for the Ru thin film layer as a promising buffer layer for HTS applications and electrode materials in memory devices.

2. Experimental procedure

In this experiment, bis-(ethyl-π-cyclopentadienyl)ruthenium was used as the precursor, which is yellow liquid at room temperature. Tetrahydrofuran was used as the solvent to dissolve the precursor. The molar concentration of the solution was maintained at 0.1 M. The decomposition temperatures were determined by thermal analyses, such as differential scanning calorimetry (DSC) (Mac. Science DSC-3110) and a thermogravimetric analysis (TGA), combined with mass spectroscopy and Fourier transform infrared spectroscopy (FTIR) measurements. Biaxially textured Ni substrates were obtained from randomly oriented high-purity (99.9%) Ni sheets, which were first mechanically deformed by rolling and then were made into Ni tapes of 80 μm in thickness and 10 mm in width. Ni tapes were annealed in a vacuum chamber at 800 °C, the mixed gases of H_2 (10%) and Ar (90%) were flown into the chamber and the base pressure was kept to around 100 mTorr. The velocity of the Ni tapes was kept to about 1 cm min^{-1}. The MOCVD apparatus consisted of a vertical warm-wall reactor and a resistive substrate heater. The experimental conditions are summarized in Table 1. All of the lines to the reactor were heated to 120 °C to prevent the vaporized precursor from condensing in transit. After repeated deposition runs, the lines and vaporizers were free of residues or deposits, which ensured excellent repeatability of the depositions. A film phase analysis and resistivity measurements were performed by X-ray diffraction (XRD) using a Rigaku D/Max-B diffractometer with Cu Kα radiation and a four-point probe, respectively. The thickness of the film and surface morphology were observed by cross-sectional scanning electron microscopy (SEM) and atomic force microscopy (AFM). Auger electron spectroscopy (AES) was also used to measure the relative atomic concentration to confirm the variations in composition and surface electronic state, using a Perkin-Elmer phi 400 scanning Auger microprobe.

Table 1
Deposition conditions of Ru thin films on Ni substrate by MOCVD

Precursor	$Ru(EtCp)_2$
Bubbler temperature (°C)	120
Reaction gas O_2 flow rate (sccm)	0–40
Carrier gas Ar flow rate (sccm)	10–100
Substrate	Ni(2 0 0)
Line temperature (°C)	120
Deposition temperature (°C)	300–500
Deposition pressure (Torr)	0.02–0.2
Deposition time (min)	30

3. Results and discussion

Fig. 1 shows the TGA results analyzed under O_2 and Ar atmosphere. The precursor began to lose weight near 80 °C regardless of the atmosphere, and the precursor decomposed at 200 °C under O_2 atmosphere. This also demonstrates that the weight loss, at 6.3%, results from the endothermic processing between 100 and 200 °C. No more weight loss occurred above 200 °C. This shows the Ru source should be completely decomposed. There are no obvious changes for the Ru source under different atmospheres, even after it has been stored for 3 months. The thermal analysis with time was carried out using differential scanning calorimetry in 200 sccm oxygen or argon. The Ru source was heated up to 300 °C and cooled down to room temperature at a rate of

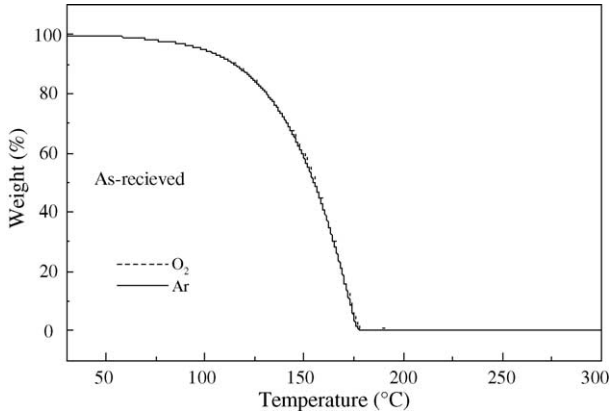

Fig. 1. TGA curves of the precursor under oxygen and argon. The inset shows the weight loss (%) as temperatures increase.