Thin Solid Films 589 (2015) 673–680

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Nanometer-thick copper films grown by thermal atomic layer deposition

Zhenyu Zhong [a,b], Xiuqin Wang [a,b,c], Jianning Ding [a,b,c,*], Ningyi Yuan [a,b,**]

[a] Jiangsu Collaborative Innovation Center for Photovoltaic Science and Engineering, The School of Materials Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China
[b] Jiangsu Key Laboratory for Photovoltaic Engineering and Science, Changzhou University, Changzhou 213164, Jiangsu, China
[c] Micro/Nano Science and Technology Center, Jiangsu University, Zhenjiang 212013, China

ARTICLE INFO

Article history:
Received 4 March 2015
Received in revised form 11 June 2015
Accepted 18 June 2015
Available online 2 July 2015

Keywords:
Nanometer-thick copper film
Thermal atomic layer deposition
Electrical property

ABSTRACT

Because of the superior properties of copper, it has been of great interest as a conducting material to replace aluminum in device manufacturing. In this study, we investigated the influence of substrate temperature, film thickness, and rapid thermal annealing (RTA) on the deposition of Cu films of thickness less than 10 nm. Compared to thicker films, the electrical properties of nanometer-thick films were found to be very sensitive to the deposition temperature. Further, we determined the optimal deposition temperature to obtain low-resistivity nanometer-thick Cu films. The Cu films were deposited with island-type growth, and the interconnection between grains plays a major role in the resistivity of the films. We also determined the critical thickness at which Cu films exhibit continuous growth as 8 nm. After RTA, the film color darkened, electron scattering became weak, and the resistivity reduced more than 20% with annealing at 300–350 °C, because of the growth of Cu grains. The results of this study indicate that thermal ALD can be used in conjunction with RTA to produce low-resistivity Cu thin films, the thickness, uniformity, and conformality of which can be easily controlled.

1. Introduction

Copper has been of great interest as a conducting material since 1997 [1]. The electrochemical deposition of copper metal for this application took nearly ten years to develop [2]. Because of its good conductivity, low temperature coefficient of resistance, thermal stability, and superior resistance to electromigration and stress migration in comparison with aluminum, copper can replace aluminum in device manufacturing [3–6]. The incorporation of conformal nanometer-thick copper layers has been in high demand in the modern electronics industry for use as, for example, a seed layer for the subsequent electrodeposition of Cu in interconnects [7].

Typically, Cu films have been prepared by electrodeposition, physical vapor deposition (PVD), and chemical vapor deposition (CVD). Compared with other PVD methods such as sputtering, evaporation, and CVD methods, the atomic layer deposition (ALD) method provides excellent ability to control uniformity, conformality, and thickness [8–14]. Therefore, the ALD method is particularly suitable for depositing nanometer-thick Cu films. Some studies have reported on the ALD of Cu thin films using various reactant precursors [15–23] especially the $ZnEt_2$ which has been used as a reducing agent [24,25]. There are two approaches to ALD: thermal ALD and plasma-enhanced ALD (PEALD). The lowest reported resistivity of 10-nm-thick Cu films was 52 μΩ cm for deposition using PEALD [26], while the resistivity of a 10-nm-thick Cu film deposited using thermal ALD was reported to be greater than 250 μΩ cm [27]. In general, the resistivity of Cu films prepared using thermal ALD is only slightly higher than that of Cu films prepared using PEALD.

There has been no systematic study on Cu films of thickness less than 10 nm. In this paper, because thermal ALD equipment is simpler and cheaper than PEALD equipment, thermal ALD was chosen to deposit Cu thin films. We investigated the influence of substrate temperature, film thickness, and rapid thermal annealing (RTA) on the deposition of Cu films of thickness less than 10 nm.

2. Experimental section

The ALD equipment (TFS: 200, BENEQ Co., Finland) was used to deposited Cu film. Copper (II)-hexafluoroacetylacetonate $[Cu(hfac)_2]$ was used as the Cu source, and optical glass (Yinxing Optical Co., Ltd, China) was used as substrates. Cu thin films were deposited onto substrates using $[Cu(hfac)_2]$ and diethylzinc ($ZnEt_2$) as ALD precursors. High-purity nitrogen served as both the carrier and purging gas. The N_2 flow rate was 300 $cm^3\ min^{-1}$. $ZnEt_2$ and $[Cu(hfac)_2]$ were evaporated at 20 °C and 70 °C, respectively. The process cycle consisted of exposure to $[Cu(hfac)_2]$ for 800 ms, purging with N_2 for 4 s, exposure to $ZnEt_2$ for 300 ms, and purging with N_2 for 2 s. The Cu thin films were grown at temperatures of 180 °C–200 °C under a pressure of 4 mbar. After ALD, the samples were annealed at 300 °C–400 °C for 1 min in an RTA furnace using a mixture of Argon (85%) and hydrogen (15%) as the reducing gas.

---

* Correspondence to: J. Ding, Jiangsu Collaborative Innovation Center for Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China.
** Correspondence to: N. Yuan, Jiangsu Key Laboratory for Photovoltaic Engineering and Science, Changzhou University, Changzhou 213164, Jiangsu, China.
E-mail addresses: dingjn@cczu.edu.cn (J. Ding), nyyuan@cczu.edu.cn (N. Yuan).

http://dx.doi.org/10.1016/j.tsf.2015.06.053
0040-6090/

X-ray photoelectron spectroscopy (XPS) (Quantera, ULVAC-PHI Co., US) was used to analyze the compositional data. X-ray diffraction (XRD) (D/MAX Ultima III, Rigaku Corporation, Tokyo, Japan) was performed to determine the crystallinity of the Cu films. The morphology was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi, Japan), and the thickness was measured using a profilometer (DEKTAKII) and confirmed using cross-sectional FE-SEM. The resistivity was measured by four-point probe (Keithley Co., US).

3. Results and discussion

3.1. Growth rate and growth mode of copper films deposited by thermal ALD

In a true ALD process, the surface reactions must be self-terminating and complementary in order to yield a uniform, conformal, and high-quality copper metal thin film. To verify that the surface reaction for [Cu(hfac)$_2$] is really self-terminating, the dose time was varied between 100 ms and 1 s at growth temperatures of 180–200 °C. The film thickness per cycle for [Cu(hfac)$_2$] is saturated when the pulse time exceeds 400 ms, as shown in Fig. 1(a). This result indicates that [Cu(hfac)$_2$] undergoes a self-terminating reaction with the copper metal surface prepared by reaction with diethylzinc. Fig. 1(b) shows that the growth rate as a function of the ZnEt$_2$ dose time is saturated when the pulse time exceeds 0.5 s. This result suggests that ZnEt$_2$ undergoes a fast self-terminating replacement reaction with [Cu(hfac)$_2$] adsorbed on substrates. All the self-terminating growth experiments were undertaken with 300 cycles and resulted in the deposition of 42 nm thick films. The thickness of the copper thin films versus the number of ALD cycles is shown in Fig. 1(c). The thickness is linear with respect to the number of cycles, showing that the surface reactions for this ALD process are complementary and complete. The measured growth rate was 0.14 nm per cycle.

XPS analysis was performed to determine the composition of the copper films grown by this ALD process as a function of ALD temperature. Fig. 2(a–b) shows the typical survey and high-resolution spectra of the copper films grown at 180–200 °C. The XPS of the copper films cleaned by Ar$^+$ ion sputtering display the strong photoelectron and Auger electron peaks for Cu with a very weak peak from Zn and the content of zinc is ~0.30%. The strong peaks of Cu(2p) and Cu(LMM) (LMM: transition between inner shells L and M) clearly demonstrate that the films are almost pure copper metals. The peaks in the XPS show almost same shapes and intensities between 180 and 200 °C. These observations indicate that ALD surface reactions have a process window temperature in the range of 180–200 °C, in accordance with the dependence of growth rate per cycle on deposition temperature (Fig. 1d). When the ALD temperature is raised to 210 °C, obvious Zn peaks appear as shown in Fig. 2(f) and the content of zinc is 2.32%. The comparison of Fig. 2(c) and (f) indicates that the Zn(2p) peak rapidly increases in intensity with the increase of the substrate temperature (Fig. 2(d)). These changes indicate that zinc compounds are decomposed and incorporated into the copper films above 200 °C. Also, at a temperature below 180 °C, the growth rate decreases (Fig. 1(d)) and the copper films are contaminated with zinc. The window temperature for ALD process is very narrow at between 180 and 200 °C; the lower limit is dictated by desorption of the zinc compounds and the upper limit by their decomposition.

To investigate the influence of thickness on the resistivity of Cu films, the growth mode of the Cu films must be determined. The morphology of the deposited films was examined using SEM as a function of growth cycles (film thickness), as shown in Fig. 3(a–d), which shows that the growth mode of Cu films is an island-type. With the increase in film

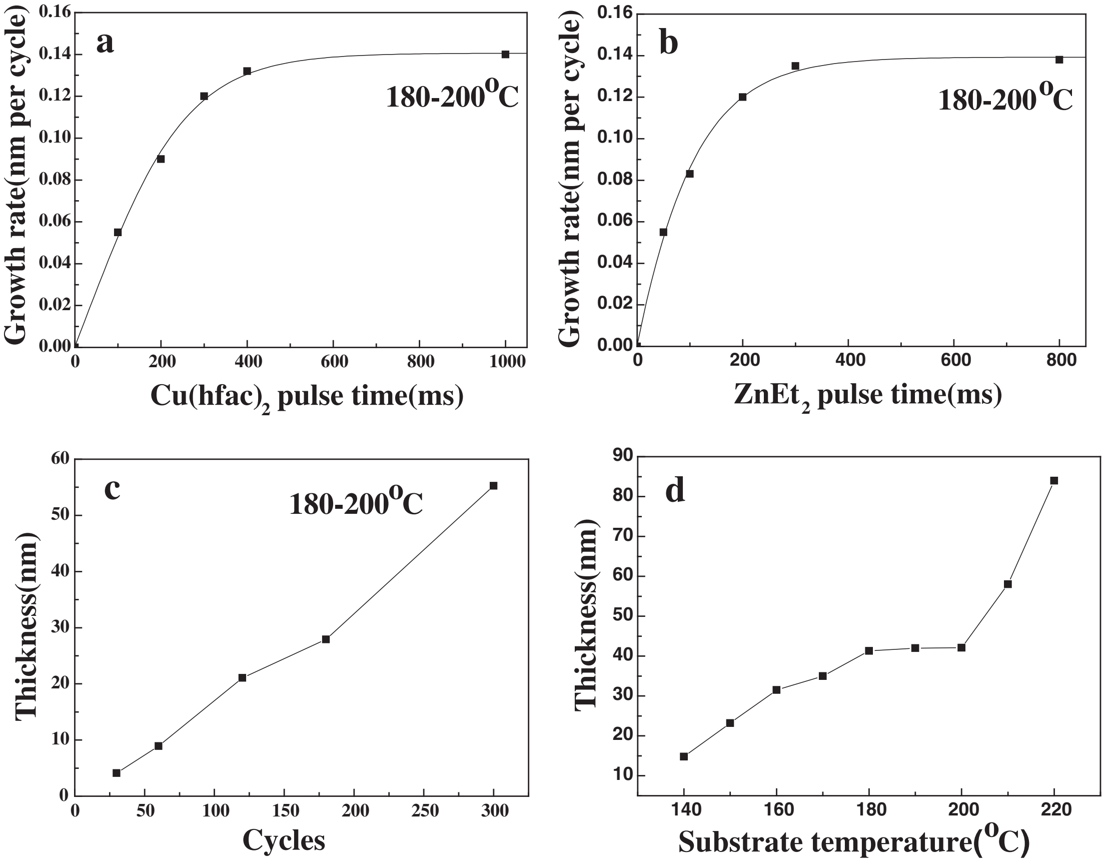

Fig. 1. (a–d) Growth rate (a) as a function of [Cu(hfac)$_2$] pulse time at 180–200 °C and (b) as a function of ZnEt$_2$ pulse time at 180–200 °C. Thickness of the copper films (c) versus the number of ALD cycles at 180–200 °C, (d) versus the substrate temperature.