Applied Surface Science 328 (2015) 374–379

Contents lists available at ScienceDirect

Applied Surface Science

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

The role of oxygen in the deposition of copper–calcium thin film as diffusion barrier for copper metallization

Zhinong Yu [a,*], Ruihuang Ren [a], Jianshe Xue [b], Qi Yao [b], Zhengliang Li [b], Guanbao Hui [b], Wei Xue [a]

[a] School of Optoelectronics and Beijing Engineering Research Center of Mixed Reality and Advanced Display, Beijing Institute of Technology, Beijing 100081, China
[b] Beijing BOE Optoelectronics Technology Co., Ltd, Beijing 100176, China

ARTICLE INFO

Article history:
Received 27 July 2014
Received in revised form
11 December 2014
Accepted 13 December 2014
Available online 19 December 2014

Keywords:
Copper metallization
Copper–calcium alloy
Resistance
Adhesion
Diffusion

ABSTRACT

The properties of copper (Cu) metallization based on copper–calcium (CuCa) diffusion barrier as a function of oxygen flux in the CuCa film deposition were investigated in view of adhesion, diffusion and electronic properties. The CuCa film as the diffusion barrier of Cu film improves the adhesion of Cu film, however, and increases the resistance of Cu film. The introduction of oxygen into the deposition of CuCa film induces the improvement of adhesion and crystallinity of Cu film, but produces a slight increase of resistance. The increased resistance results from the partial oxidation of Cu film. The annealing process in vacuum further improves the adhesion, crystallinity and conductivity of Cu film. X-ray diffraction (XRD) and Auger electron spectroscopy (AES) show that the CuCa alloy barrier layer deposited at oxygen atmosphere has perfect anti-diffusion between Cu film and substrate due to the formation of Ca oxide in the interface of CuCa/substrate.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, with the rapid development of very-large-scale integrated (VLSI) circuits and high-resolution thin film transistor liquid crystal displays (TFT-LCDs), the application of Cu metallization becomes more and more popular due to its low resistivity, however, and is limited for the significant inter-diffusion between Cu and Si atoms and the poor adhesion of Cu film. Such Cu metallization requires an extra barrier layer at the interface to prevent Cu interdiffusion with silicon based materials and improve the poor adhesion of Cu film [1–6].

It has been extensively reported that refractory metals such as Ta, Ti, Zr, Mo, Cr and Ru can be used as a perfect barrier in Cu metallization, in particular, Ta/TaN barrier system has been put into VLSI circuit applications, and molybdenum or titanium has conventionally been employed as a buffer layer in a bilayer structure of Cu/Mo or Cu/Ti in TFT-LCDs [7,8]. However, these heterogeneous metal bilayer structures give rise to problems in wet etch patterning due to the differences in electrochemical properties between Cu and the refractory metals. In addition, the process needs high temperature annealing for the formation of buffer layer or the improvement of adhesion. Furthermore, relatively high material price as Mo and Ti increases production cost.

In recent years, considerable attention has been focused on a technique using Cu–Mn alloy that allows the self-forming of a layer that prevents diffusion and aids adhesion as a reliable and cost-effective alternative to an extra layer of Mo or Ti [9,10]. With this technique, Cu–Mn alloy is first deposited directly on oxygen-containing material such as silicon oxide or glass. During subsequent annealing, Mn migrates toward the interface and reacts with a surface oxide layer until a Mn complex oxide layer forms, which strengthens adhesion and blocks diffusion. However, a technical problem in attempting to apply Cu–Mn alloy to source/drain interconnects is a lack of oxygen at the interface between the Cu–Mn alloy and phosphorus doped hydrogenated amorphous silicon (n-type α-Si:H). To overcome this problem, surface oxidation pretreatment of the n-type α-Si:H is required before depositing the alloy. Junichi Koike adopted a 10 nm SiO_2 grown by oxide plasma pretreatment of n-type α-Si:H surface to improve the adhesion and diffusion barrier of Cu–Mn electrode. However, forming an additional oxide layer in a current pathway of TFT may increase the parasitic resistance and degrade its electrical properties [11].

In this paper, Cu–1 at% Ca alloy thin film was used as a diffusion barrier for copper metallization, and the properties of Cu film as

* Corresponding author. Tel.: +86 1 68913259 11.
E-mail address: znyu@bit.edu.cn (Z. Yu).

http://dx.doi.org/10.1016/j.apsusc.2014.12.087
0169-4332/© 2014 Elsevier B.V. All rights reserved.

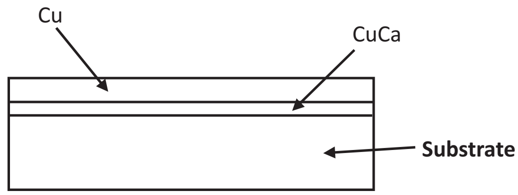

Fig. 1. Diagram of the sample structure.

a function of oxygen flux in the CuCa film deposition were investigated in view of adhesion, diffusion and electronic properties in order to develop the applications of Cu interconnects in VLSI or TFT circuits.

2. Experimental details

The float glass was used as the substrate. Prior to deposition, the substrates were first cleaned by ultrasonic technology with alcohol, acetone and deionized water in sequence, to remove organic contaminants. Then, the wafers were dried by nitrogen. CuCa film and Cu film were successively deposited on the substrates by magnetron sputtering using Cu–1 at% Ca alloy target (99.999% purity) and Cu target (99.999% purity), respectively. Diagram of the sample structure is shown in Fig. 1. The single-layer CuCa film and Cu film were also prepared for analysis of the film properties. The deposition atmosphere of CuCa thin film was oxygen/argon (O_2/Ar) mixture gas, and the deposition pressure was set to 0.5 Pa. The O_2 gas flow rate varied from 0 to 5 sccm, and the substrate temperature was 100 °C. The thickness of CuCa thin film as buffer layer was chosen from 5 nm to 50 nm. The deposition atmosphere of Cu thin film was Ar gas, and the deposition pressure was set to 0.3 Pa. The thickness of Cu film was kept same as 300 nm, and the substrate temperature was room temperature. The samples were annealed at 400 °C for an hour in vacuum.

The crystalline structure of thin film was determined by X-ray diffraction (XRD) measurement using Cu Ka radiation. The sheet resistance was measured by the four-point probe (FPP) technology. The scan electron microscope (SEM) was employed to characterize the cross-section morphology as well as the evolution of the microstructure of film system. The depth profile was obtained with Auger electron spectroscopy (AES) using a probing energy of 10 kV and 10 nA corresponding to a beam size of 20–25 nm.

The film adhesion was measured by means of the hundred grid knife scratching methods and classified as six grades as 5B, 4B, 3B, 2B, 1B and 0B according to the area percentage for removal of coating from the substrate after scratching. The 5B indicates no coating removal and the best adhesion. The 4B, 3B, 2B, 1B and 0B correspond to coating removal of less than 5%, 5–15%, 15–35%, 35–65% and more than 65%, respectively [12].

3. Results and discussion

The poor adhesion of Cu film deposited on glass or silicon has been confirmed, and some methods were proposed to enhance the adhesion in view to the formation of an oxide layer by an inset of buffer layer and a high temperature annealing process [1–10]. Copper oxidizes easily in an oxygen atmosphere [13], and calcium has a low solubility in copper and a higher oxidation tendency than copper [14]. Calcium is added to the copper film and copper–calcium alloy film as a buffer layer of Cu film deposition could be advantageous to the improvement of Cu film properties. In the experiments, the Cu film adhesion was improved with an inset of CuCa buffer layer prepared at an optimal deposition condition. Among the deposition parameters of CuCa buffer layer, the oxygen flux remarkably affects the adhesion and resistance of Cu films. It was experimentally found out that the introduction of oxygen into the deposition of CuCa film is necessary to improve the adhesion of Cu film; and the adhesion is perfect even when the CuCa film is grown at room temperature. The Cu/CuCa double layers peel off when the CuCa film is deposited without oxygen introduction, even at high temperature.

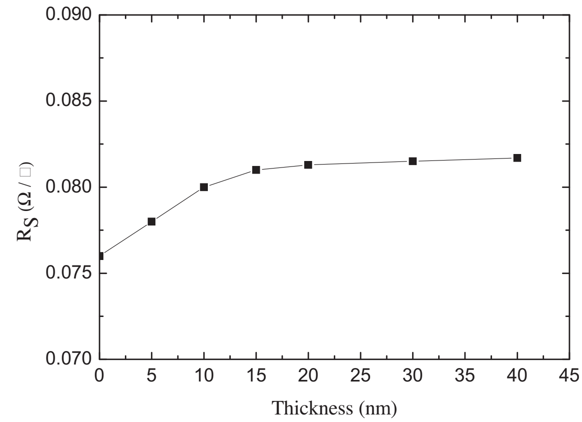

Fig. 2. The dependence of sheet resistance of Cu/CuCa/glass on the thickness of CuCa buffer layer.

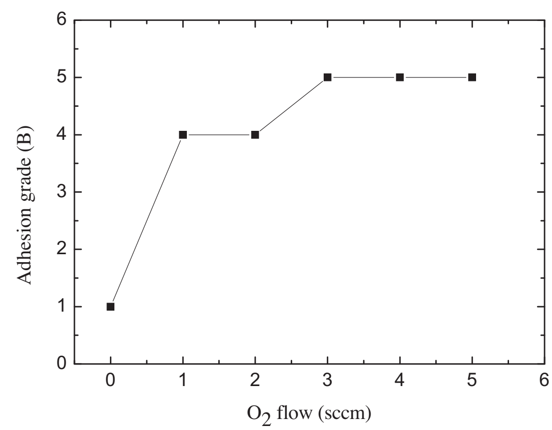

Fig. 3. The effects of oxygen flux in depositing CuCa buffer layer on the adhesion of Cu/CuCa/glass.

Fig. 2 shows the sheet resistance of Cu/CuCa/glass samples as-deposited with various thickness CuCa buffer layer. The oxygen flux in depositing CuCa buffer layer was kept as 2 sccm. The resistance of sample without CuCa buffer layer or Cu/glass sample is 0.076 Ω/□. The resistance has a fast increase from 0.076 Ω/□ to 0.081 Ω/□ with an introduction of very thin buffer layer, however, and increases slightly with the increasing thickness of buffer layer when the thickness exceeds some value as 10 nm. The total resistance of a bilayer is a combination of the resistances of two consecutive layers in parallel as follows: $1/R_{Total} = 1/R_{Cu} + 1/R_{CuCa}$. Since R_{Cu} is much less than R_{CuCa}, the total resistance R_{Total} would mainly depend on the Cu layer. The increased resistance indicates that the CuCa buffer layer affects the Cu film deposition in succession; otherwise, the resistance should be decreased after the introduction of CuCa layer. The adhesion of sample without CuCa buffer layer or Cu/glass sample is 0B, which is the worst adhesion in this test. The film adhesion is perfect for the samples with various thickness CuCa buffer layer and the adhesion grade is 5B or 4B.

Fig. 3 shows the effects of oxygen flux in depositing CuCa buffer layer on the adhesion of Cu/CuCa/glass samples as-deposited. The adhesion grade is 1B for the sample prepared without oxygen introduction into the deposition of CuCa film, and 4B or 5B for those

Download English Version:

https://daneshyari.com/en/article/5348845

Download Persian Version:

https://daneshyari.com/article/5348845

Daneshyari.com