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CRYSTALLIZATION AND FAILURE BEHAVIORS OF Ta-Co NANOSTRUCTURED/AMORPHOUS DIFFUSION BARRIERS FOR COPPER METALLIZATION

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Abstract. This work examines the thin-film properties and diffusion barrier behaviors of thin Ta-Co films, aiming at depositing highly crystallization-resistant and highly conductive diffusion barriers for Cu metallization. Structure analyzing indicates that the deposited Ta-Co films indeed have a glassy structure and are free from highly resistive intermetallic compounds, thus giving a low resisitivity under 20 μΩ-cm. Examining Si/Ta-Co/Cu stacked samples by using 4-point probes and XRD reveals that thermally induced failure of amorphous Ta-Co barriers are triggered by the barrier's crystallization at temperatures just under around 600 °C. The effectiveness of the nanostructure/amorphous Ta-Co thin film thus can be substantially enhanced by effectively blocking diffusion of copper towards the underlying silicon.

1. INTRODUCTION

As integrated circuits scale down, Cu (ρ ~1.67 μΩ-cm) has replaced Al-Cu (ρ ~2.7 μΩ-cm) alloy for metallization interconnection owing to its lower resistivity and higher electromigration resistance [1,2]. However, Cu atoms diffuse readily into SiO_2 and Si induce a degradation of transistor reliability by forming particular impurity level in the silicon [3]. A particular diffusion barrier layer is therefore required to suppress Cu atom from diffusion into transistor regions. Reactively sputtered TiN thin film is usually adopted as diffusion barrier on traditional Al-Cu metallization. Since the solid solubility between Al and Si is quite low (<1.59 at.%), TiN diffusion barrier layer mostly failure owing to TiN decomposition and react with Si to form $TiSi_2$ at an elevated temperature. For Cu metallization, however, highly reactivity between Cu and Si induce Cu_3Si and/or CuO formation at 200-300 °C. Thus, dielectric materials degradation cause a circuit short on interconnection of Si(SiO_2)/Cu [4,5]. Many approaches has been carried out by using various metals and compounds as Cu diffusion barrier such as Ta(N) [6,7], Ta-Si(N) [8], W, Cr, Ti, Mo [9]. Among these studies, Ta-based thin films are frequently adopted as diffusion barrier to prevent Cu from diffusion owing its superior characteristics.

Binary or ternary Ta-based polycrystalline thin films are frequently used as a barrier layer to prevent Cu from diffusion. Their grain boundaries, however, tend to act as the main diffusion paths for copper atoms to penetrate the diffusion barrier, causing the failure of silicon/copper interfaces or generating deep-level recombination centers in dielectrics. In addition to the needs of low resistivity and high thermal stability, therefore, diffusion barrier layers with an amorphous structure are more promising due to the lack of the grain boundary [10]. In particular, binary amorphous alloys such as refractory metal-silicon alloys and nitrogen-containing ternary amor-

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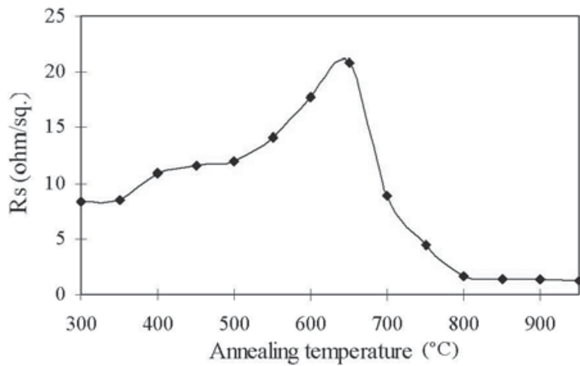

Fig. 1. Sheet resistance as a function of annealing temperature for Ta-Co/Si thin films.

phous alloys frequently exhibit superior barrier properties for Cu metallization [11]. Amorphous thin films thus are potentially more promising than crystalline Ta and TaN thin films as the lack of grain boundaries [12]. A survey of the available literature indicates that Ta-TM binary alloy (TM = Fe, Co, Ni) preparing by mechanical alloying has a capability of amorphization and a high crystallization temperature [13]. An amorphous Ta-Co/Si thin film has also performed by co-deposition to evaluate its phase formation [10]. A crystallization temperature of 600 °C for amorphous Ta-Co thin film can be observed. Therefore, this work examines the thin-film properties and diffusion barrier behaviors of thin Ta-Co e-beam evaporated films, aiming at depositing highly crystallization-resistant and highly conductive diffusion barriers for copper metallization. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) indicate that the deposited Ta-Co films indeed have a glassy structure and are free from highly resistive intermetallic compounds, thus giving a resisitivity as low as under 20 $\mu\Omega$-cm.

2. EXPERIMENTAL

$Ta_{50}Co_{50}$ (at.%) alloy was prepared by an arc melting method for several times under high purity argon protection to ensure its homogeneous. p-type Si wafers of (100) orientations were used as substrate by a standard RCA cleaning process prior to load into electron gun evaporation chamber. Electron beam evaporation onto the Si substrate was performed at a base pressure of under $5 \cdot 10^{-6}$ Torr. The deposition rate was controlled at 0.1 nm/sec, which was monitored by a quartz vibration controller. The films were heat-treated in a rapid thermal vacuum annealer in protective argon ambient at temperature from 300 to 950 °C. Electrical resistivity of the films was obtained from the films' thickness and sheet resistance, obtained from a four-point probe measurement. The films were examined by x-ray diffraction (XRD) and transmission electron microscopy (TEM) to elucidate the phase formation and structure.

3. RESULTS AND DISCUSSION

3.1. Crystallization behavior of Ta-Co/Si

Sheet resistance variation associated with the annealing temperature of Ta-Co(50 nm)/Si thin film was adopted to elucidate the kinetic of crystallization by a well-developed model [14]. Fig. 1 displays the sheet resistance dependence of the annealing temperature range from 300 to 950 °C for 5 minutes. The sheet resistance was initially increased with increasing annealing temperature, reached a maximum value of 21 ohm/sq. (resistivity of 17.55 $\mu\Omega$-cm), then decreased with further increasing annealing temperature. Post annealing above 800 °C/5min, a low and stable sheet resistance of around 1.3 ohm/sq. was obtained.

Structure analysis (not shown here) indicated an amorphous/nanocrystalline structure was obtained for as-deposited and post annealed Ta-Co/Si thin films below 500 °C. Post annealed above 500 °C, a tiny Co_2Ta phase diffraction peak was detected, which revealed the crystalline grain was very tiny with an average grain size of 7.5 nm from TEM observation. In addition to Co_2Ta phase, a Co_2Si phase was also detected for post annealing above 500 °C owing to the reaction of Ta-Co thin film with the silicon substrate because of the low reaction temperature of Co and Si. From XRD and sheet resistance analysis, the crystallization temperature was 500 °C. Above 500 °C, more crystallization Co_2Ta and Co_2Si phase formations induced a decline in sheet resistance. For post annealed at 900 °C /5min, a nanostructured grain can be observed with an average grain size of 11.3 nm.

The change in sheet resistance during Ta-Co crystallization can be related to the progress of the transformation by using a resistance model

$$X_{trans}(t)=[R(0)-R(t)]/[R(0)-R(f)], \quad (1)$$

where X_{trans} is the volume fraction of the crystallized phase, $R(0)$ is the initial film sheet resistance of the amorphous phase, $R(f)$ is the final saturated film resistance of the crystallized Ta-Co film and $R(t)$ is the time-dependent film resistance. An increasing trend can be obtained in plotting the fraction of crystallization structure as a function of normalized an-

nealing time at 500-600 °C. Normalized sheet resistance increased with increasing annealing durable time in a sigmoidal indicated the crystallization involving nucleation and growth mechanism. Sheet resistance increased with increasing post annealing temperature and endured time were associated with increasing the crystallization volume.

A well-developed Johnson-Mehl-Avrami kinetic analysis was used to deduce the effective crystallization activation energy. The general equation is in the form of:

$$X_{trans}(t)=1-\exp(-kt^n)\,, \qquad (2)$$

where k is a Avrami coefficient, n is Avrami exponent. By defining the time at which crystallization is 50% complete as $\tau_{0.5}$, and

$$\tau_{0.5} = \tau_0 \exp\,(E_{ac}/kT) \qquad (3)$$

the effective activation energy E_{ac} for the crystallization can be deduced from Eq. (3). The slope of $\ln(\tau_{0.5})$ versus $1/kT$ was 2.358 eV, as shown in Fig. 2, is the effective crystallization activation energy of Ta-Co thin film.

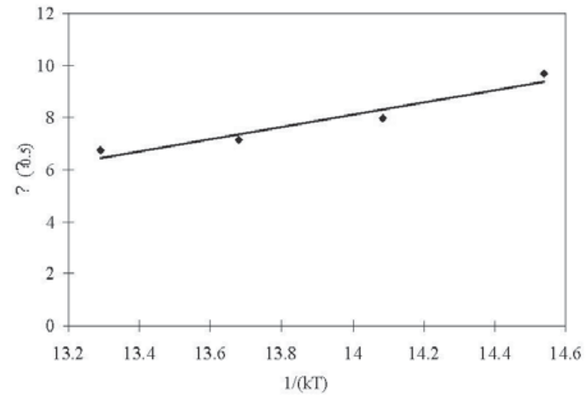

Fig. 2. Plot of $\ln(\tau_{0.5})$ vs.$1/kT$ to determine to activation energy for the crystallization.

Fig. 3b shows the evolution of x-ray diffraction patterns as a function of annealing temperature of Cu/Ta-Co(50nm)/Si thin films. For post annealing below 500 °C, only a tiny and broaden Ta diffraction peak at 37.4° can be found, which depicted that a small amount of Ta nanocrystalline structure was

3.2. Cu/Ta-Co/Si failure behavior

A four-point probes system was employed to measure the relative change in sheet resistance of the post annealed Cu/Ta-Co/Si thin films to identify the failure behavior. The relative change in sheet resistance ($\Delta R/R_0$) with annealing temperature of Cu/Ta-Co(20, 50, 100 nm)/Si was shown in Fig. 3a. The three curves exhibited a similar trend. $\Delta R/R_0$ increased slowly at a low annealing temperature and then increased sharply at a specified elevated temperature. Referred to curve in Fig. 3a, constant low $\Delta R/R_0$ was obtained for post annealed Cu/Ta-Co(20 nm)/Si below 500 °C /5min and raised abruptly as temperature above 500 °C /5min. Correspondingly, Cu/Ta-Co(50 nm)/Si and Cu/Ta-Co(100 nm)/Si thin films showed a sharp increased at 550 °C /5min and 600 °C /5min, respectively. Since the sharp increases in resistivity of Cu/Ta-Co/Si indicated serious intermixing and chemical reactions among Si, Ta-Co, and Cu, and thus degraded the metallization layers. Apparently, thicker Ta-Co thin film exhibited a better barrier effect since the failure temperature increased with increasing the thickness of Ta-Co barrier layer. Failure temperature of 550 °C can be obtained for Cu/Ta-Co(50nm)/Si thin films, which is slightly higher than that of 500 °C for 50nm TaN barrier layer [15]. Ta-Co thin film is therefore more promising on Cu metallization as diffusion barrier layer.

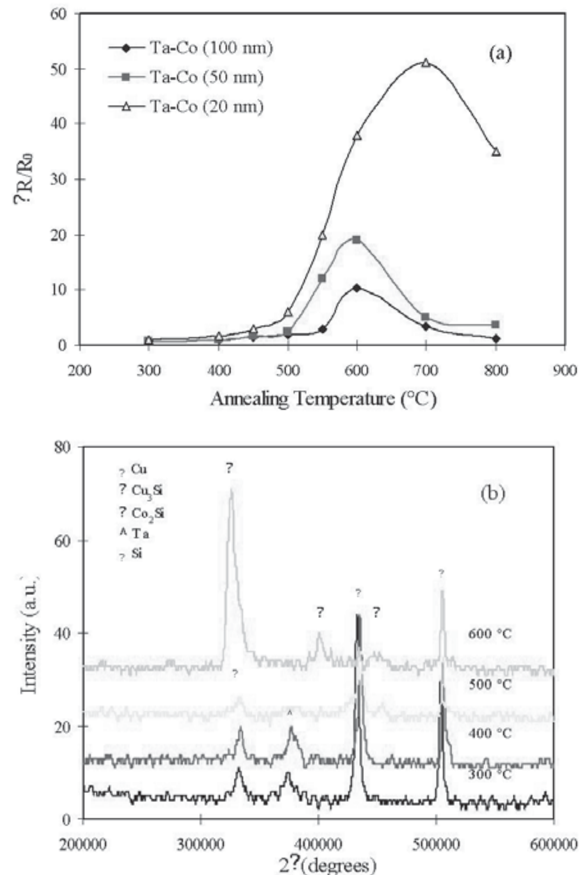

Fig. 3. (a) Relative changes in sheet resistance, (b) Evolution of x-ray diffraction patterns, of Cu/Ta-Co/Si thin films by annealing at various temperatures for 5 min.

obtained for Cu/Ta-Co(50nm)/Si thin films. However, only crystallized Co_2Ta phase can be traced at 500 °C for Ta-Co (50nm)/Si thin films. Cu deposited onto Ta-Co/Si thin film led to an early crystallization of nanostructured Ta grains. For post annealed Cu/Ta-Co(50nm)/Si thin films above 600 °C /5min, two tiny Cu_3Si diffraction peaks can be examined depicting the Cu atoms pass through Ta-Co barrier and reacted with underlying Si substrate, which induced the Ta-Co barrier layer failed to prevent Cu diffusion. Therefore, Cu_3Si phase formed at interface between Ta-Co and Si substrate. Failure temperature of 550 °C for Cu/Ta-Co(50nm)/Si thin films evidenced from relative sheet resistance change can be summarized, which are slightly higher than that of crystallized temperature of 500 °C for Ta-Co(50nm)/Si thin films.

4. CONCLUSION

Amorphous/nanostructured Ta-Co thin films were prepared by electron beam evaporation and acted as a diffusion barrier for Cu metallization. As deposited Ta-Co film was amorphous and remain stable up to around 500 °C. Crystallization activation energy for Ta-Co amorphous thin film was 2.358 eV according to Johnson-Mehl-Avrami method. The first phase to crystallized was Co_2Ta and Co_2Si phases at 500 °C. All Ta-Co thin films prevent the formation of the cooper silicide up to the high temperature above their crystallization temperature. The Cu/Ta-Co(50nm)/Si thin films barrier effect was failure at 550 °C. The failure temperature was slightly higher than the crystallization temperature of Ta-Co thin film can be concluded. The effectiveness of the nanostructure/amorphous Ta-Co thin film thus can be substantially enhanced by effectively blocking diffusion of copper towards the underlying silicon.

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