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The thermal stability of 7 nm Ti, Pt, and Ru interfacial adhesion layers between Cu film (10 nm) and a Ta barrier layer (4 nm) has been investigated. The barrier properties and interfacial stability have been evaluated by Rutherford backscattering spectrometry (RBS). Atomic force microscopy was used to measure the surfaces before and after annealing, and all the surfaces are relatively smooth which excludes islanding or dewetting phenomena as a cause of the instability. The RBS showed no discernible diffusion across the adhesion layer/Ta and Ta/Si interfaces which provides a stable underlying layer. For a Ti interfacial layer, RBS indicates that during 400 °C annealing, Ti interdiffusion is detected which is less evident than Ti. Among the three adhesion layer candidates, Ru shows negligible diffusion into the Cu film indicating thermal stability at 400 °C. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4792523]

I. INTRODUCTION

Copper has been well studied as an interconnect material in advanced metallization technology due to its resistance to electromigration and its lower resistivity compared to aluminum.^{1–5} Traditionally, interconnect structures employ Ta, TaN, or TiN as a barrier layer with a physical vapor deposition (PVD) Cu layer that serves as a seed to Cu electrochemical deposition.^{1,6,7} However, the overall thickness of the seed and barrier configuration is typically 30–40 nm (Ref. 8) which exceeds the requirement for the 32 nm integrated circuit technology node. Moreover, an ultrathin diffusion barrier (<3 nm thick and below) is needed for further scaling of the technology.⁹ Therefore, a configuration with a Cu-plateable layer and an ultrathin barrier is desirable to minimize the barrier thickness and eliminate the Cu-seed layer.

In Cu dual-damascene structures, electromigration failure occurs predominately in regions of poor adhesion,¹⁰ which indicates that Cu film stability substantially influences the failure of the devices. The reliability of interconnect structures with multilayer barrier structures is significantly determined by the stability of the bilayer interfaces.¹¹ Thus, different direct Cu plate layers have been considered including W, Pd, Ir, Os, Pt, Ru, and Ti.¹²⁻¹⁸ The stability of Cu on these layers represents the primary technical issue associated with this approach. The stability is essentially determined by interface interdiffusion and Cu film wettability on the underlying layer. In previous work, Kim et al. reported that the Cu contact angle changes after annealing for Ru and Ta substrates.¹⁷ After thermal processing, the Cu films evolved to island structures which exposed the substrates. Also Adams et al. reported detecting Ti segregated to the Cu free surface during 500 °C annealing.¹⁹ Therefore, it is necessary to investigate barrier properties and Cu wettability to determine the applicability of each direct plate material.

In a previous study, we reported that a 10 nm Cu film on a Ru substrate with a layer of native oxide tends to island after 400 °C vacuum annealing.²⁰ The islanding was driven by surface and interface energies where the reduced substrate surface energy and increased interface energy led to the island formation. In the present work, we examine both the surface morphology evolution and interfacial diffusion during annealing. Ti, Pt, and Ru are selected as adhesion layer candidates for this study. Ti has been previously investigated for improved wetting properties with Cu.²¹ Pt is a high melting point transition metal that is resistant to oxidation. As a reference, Ru is included since a cleaned Ru surface exhibits stable interfaces with Cu films upon annealing to $450 \,^{\circ}C.^{20}$

In this study, test structures have been fabricated which included a 4 nm Ta barrier layer deposited on an oxidized Si wafer. The metallic adhesion layer [Ti, Pt and Ru (7 nm)] was deposited next, followed by a 10 nm Cu film. The films were investigated before and after vacuum annealing at 400 °C. The stability of the structure was characterized by *in situ* x-ray photoelectron spectroscopy (XPS), and *ex situ* Rutherford backscattering spectrometry (RBS) and atomic force microscopy (AFM).

II. EXPERIMENT

The experiments were accomplished *in situ* using an integrated ultrahigh vacuum (UHV) system. The UHV system is maintained at $\sim 5 \times 10^{-10}$ Torr with multiple chambers interconnected through a ~ 20 m linear transfer line. The experiments in this study involve the following systems: remote H₂ plasma chamber for cleaning and vacuum annealing, electron beam evaporation for Ta, Ti, Pt, Ru, and Cu film growth, and XPS for core level analysis. After completing all *in situ* measurements, the samples were removed and analyzed with RBS for film stoichiometry and interdiffusion and AFM for surface morphology.

The samples were grown on 25 mm diameter p-type, boron doped, (100) silicon wafers with a resistivity of 0.006–0.01 Ω ·cm. The oxidized Si wafers were cleaned in an ultrasonic acetone bath for 15 min, an ultrasonic methanol bath for another 15 min, and dried with ultrahigh purity nitrogen gas. Then, the Si substrate is mounted onto a molybdenum sample holder using tantalum wires. After transferring into the UHV system, the oxidized Si (100) surfaces are cleaned using a remote H₂ plasma process.²⁰ The plasma treatment conditions are as follows: rf power maintained at 30 W, H₂ pressure of 60 mTorr, substrate at room temperature, and H₂ gas flow of 90 sccm.

To investigate the thermal stability for the different interfacial adhesion layers, a typical multilayer metalized structure was deposited on an oxidized Si substrate (Fig. 1). A 4 nm Ta barrier layer was deposited on the cleaned, oxidized Si wafer followed by a 7 nm adhesion layer (Ti, Pt, and Ru respectively), and finally, the 10 nm Cu film was deposited. The e-beam metallization system employed a Thermionics e-GUNTM evaporation source (model 100-0050) with a chamber base pressure of 4×10^{-10} Torr. For each layer, a growth rate of 0.01 nm/s was maintained with a quartz crystal thickness rate meter. After each deposition step, the samples were characterized by in situ XPS. The XPS characterization is performed at a base pressure of 5×10^{-10} Torr using a VG Clam II spectrometer operated with a Mg Ka x-ray source $(h\nu = 1253.6 \text{ eV})$. The annealing was then conducted in the plasma chamber using a tungsten irradiation filament heater located behind the sample holder. Samples were annealed for 30 min at 400 °C. During annealing, the sample was heated to constant temperature (calibrated with a Mikron-M90Q infrared pyrometer) and monitored with a Eurotherm 808 thermocouple controller. The thermocouple was located behind the center of the Si wafer. The XPS characterization was conducted again after annealing.

After *in situ* XPS characterization, the samples were removed from the UHV system for stoichiometry and morphology measurements. A separate set of samples were prepared to serve as the as-deposited films for the AFM and RBS characterization. The morphological changes of the



FIG. 1. Schematic of the multilayer structure with pertinent length scales.

TABLE I. FWHM of each peak in the RBS spectra before annealing.

	Cu	Ru	Ti	Pt	Та
FWHM (MeV)	0.026	0.027	0.036	0.025	0.023

surfaces were observed using an AgilentTM AFM model 5500. The RBS spectra were obtained using a 1.7 MV Tandem accelerator with 2.0 and 4.3 MeV He²⁺ beams. The RUMP program was utilized for simulation and interpretation of RBS spectra.²² The high energy and low energy cutoffs of each peak are represented, respectively, by projecting the tangent to the scan at its half maximum points to the energy scale axis. The full width at half maximum (FWHM) of the peaks for the as-deposited films are listed in Table I. The FWHM was slightly larger than the 0.002 MeV instrumental resolution.

III. RESULT AND DISCUSSION

A. XPS and AFM characterization

To investigate the thermal stability of Cu on the various adhesion layers, Cu/Ti/Ta, Cu/Pt/Ta, and Cu/Ru/Ta structures were deposited on oxidized Si wafers as described in Sec. II. XPS scans were carried out after the triple-layer deposition and after in situ annealing. By comparing the XPS signal from the adhesion layer (Ti, Pt and Ru) before and after annealing, we are able to identify changes in the Cu film that occur due to the underlying adhesion layer. The relative surface atomic ratio before and after annealing is shown in Table II. The surface atomic ratio is obtained from the integrated area of the XPS core levels normalized by the sensitivity factor. For Cu/Ti/Ta, the Ti 2p core level is weakly evident after Cu deposition, but after 400 °C annealing, the Ti 2p intensity increases significantly [Fig. 2(a)]. This increase in the Ti signal could indicate Cu film dewetting and exposure of the Ti layer or interdiffusion of Ti into the Cu. For Cu/Pt/ Ta, the Pt 3d core levels are not evident for the as-deposited film. But after 400 °C annealing, the 3d core level is evident, which again could indicate either islanding or interdiffusion [Fig. 2(b)]. The Cu/Ru/Ta structure does not show an increase in the Ru signal after 400 °C annealing [Fig. 2(c)], which is consistent with our previous result.²⁰

To identify if islanding occurs, the surface morphology of each sample was measured by AFM, and the results are shown in Fig. 3. All Cu surfaces appear uniformly covered although surface morphology changes are evident. The AFM images show no clearly discernible islanding or dewetting phenomena. Thus, we conclude that interfacial interdiffusion

TABLE II. XPS surface atomic ratio of the three films before and after 400 $^\circ\text{C}$ annealing.

Atomic ratio	As-deposited	400 °C annealing	
Ti/Cu	< 0.02	5.85	
Pt/Cu	_	0.79	
Ru/Cu	_	< 0.01	





Fig. 2. (Color online) XPS scans of (a) Ti 2p core levels for 10 nm Cu on Ti; (b) Pt 3d core levels for 10 nm Cu on Pt; (c) Ru 3d core levels for 10 nm Cu on Ru. Each frame shows scans before and after vacuum annealing at $400 \,^{\circ}\text{C}$.

occurs during annealing of the structures with Ti or Pt adhesion layers.

B. RBS analysis

Figure 4 shows the RBS spectra of a Cu/Ti/Ta structure before and after 400 °C annealing. The spectrum of the as-deposited sample shows well separated Ti, Cu, and Ta peaks. After annealing, the Ta peak is essentially unchanged,

indicating stable Ta/SiO_2 and Ti/Ta interfaces. The stability of these interfaces is crucial to providing a diffusion barrier layer and a smooth substrate for Cu deposition. Consequently, we can conclude that the Cu-related interface variations are due to the adhesion layer and the Cu layer.

After annealing, the high energy cutoff of the Ti peak has shifted significantly to higher energy indicating that Ti has diffused into the Cu layer. Meanwhile, the Cu peak shifts to lower energy after annealing indicating the Ti has largely accumulated on the surface. This is also supported by the XPS surface Ti/Cu atomic ratio which is over 5. After annealing, Ti and Cu interdiffuse, resulting in changes in both the XPS and RBS spectra.

The Cu/Pt/Ta system also displays evidence of interdiffusion. Since the mass of Pt and Ta are close to each other, the Ta and Pt peaks overlap in the 2 MeV spectra [Fig. 5(a)]. With higher incident ion energy (4.3 MeV), the merged peaks can be distinguished as shown in Fig. 5(b). However, due to reduced energy loss as the ions pass through the film, the higher energy spectrum has reduced sensitivity. In the 2 MeV spectrum, the high energy cutoff of the Pt peak is shifted to higher energy indicating Pt is diffusing into the Cu. This is also consistent with the XPS result. But the peak position of Cu remains almost unchanged with a slight intensity drop. In the 4.3 MeV spectra, the shape of the Cu peak does not appear symmetric because it represents two separated Cu isotope peaks (Cu⁶³ and Cu⁶⁵), and the Pt high energy edge changes slightly. Compared with the Cu/Ti/Ta system, Pt shows reduced diffusion into the Cu layer. After annealing, there is an increase of the Cu/Pt surface atomic ratio (0.79) which may indicate surface accumulation as well, but to a lesser degree than Cu/Ti.

In contrast to the results of the Ti and Pt interlayers, interdiffusion was not detected in the RBS spectra for the Cu/Ru/ Ta system (Fig. 6). All layer cutoffs are essentially aligned, and the Cu peak intensity is essentially unchanged before and after annealing. This indicates a stable interface or interdiffusion that is within the detection limit of the RBS measurement.

From the discussion above, a 4 nm Ta barrier layer has been determined to form a stable interface with oxidized Si and each of the adhesion layers at 400 °C. Ti and Pt adhesion layers exhibit interdiffusion into Cu during 400 °C annealing; however, Ru exhibits improved thermal stability.

C. Cu/Ti, Cu/Pt, and Cu/Ru interdiffusion analysis

The interdiffusion of Ti and Cu has been previously investigated by Iijima *et al.* who reported the temperature dependence of the interdiffusion coefficient in a Cu–Ti bilayer.²³ According to the Cu–Ti binary phase diagram,²⁴ Ti could react with Cu to form a range of solid solutions.^{25,26} Also, Shih *et al.* found considerable interdiffusion in the Cu/Pt system which was clearly evident in RBS spectra.²⁷ In the two systems, it was suggested that grain boundary diffusion contributes to the intermixing.²⁴ Because the annealing temperature is low compared to the Cu melting point, the transport of solvent and solute atoms is likely driven by structural defects



Fig. 3. (Color online) AFM images of 10 nm Cu on different adhesion layers: (a1) Ta/Ti/Cu as-deposited, RMS = 0.61 nm; (a2) Ta/Ti/Cu 400 °C annealing, RMS = 1.47 nm; (b1) Ta/Pt/Cu as-deposited, RMS = 0.95 nm; (b2) Ta/Pt/Cu 400 °C annealing, RMS = 0.55 nm; (c1) Ta/Ru/Cu as-deposited, RMS = 1.33 nm; (c2) Ta/Ru/Cu 400 °C annealing, RMS = 1.1 nm.

such as vacancies. The solvent and solute vacancies may arise during deposition and/or thermal annealing, and the diffusion process involves exchange of a vacancy and a neighboring solute (solvent) atom with a solvent (solute) atom.²⁴

From RBS spectra of the Cu/Pt/Ta samples, the low and high energy cutoffs of the Cu layer remain unchanged. There is a reduction of the integrated intensity of the Cu peak presumably indicating a decrease of the atomic density as Pt



Fig. 4. (Color online) He^{2+} RBS spectra (2 MeV) obtained from an as-deposited and 400 °C annealed Cu/Ti/Ta multilayer structure.

diffuses into the Cu layer. These results can be well described by the Kirkendall effect where two solids interdiffuse at different rates.²⁸ In comparison with the Cu/Pt system, the diffusion of Ti in Cu is more extensive.



Fig. 5. (Color online) (a) 2 MeV and (b) 4.3 MeV He²⁺ RBS spectra obtained from as-deposited and annealed Cu/Pt/Ta multilayer structure.



Fig. 6. (Color online) He^{2+} RBS spectra (2 MeV) obtained from an asdeposited and annealed Cu/Ru/Ta multilayer structure.

For Cu/Ru/Ta, before and after annealing, the Cu/Ru interface appears stable for annealing to 400 °C.²⁰ Ru shows negligible solubility in Cu even at 900 °C, and based on the binary phase diagram, there are no intermetallic compounds between Cu and Ru.²⁹ The stability of the Cu-Ru interface was explored using photoemission electron microscopy, where Wei et al. reported Cu diffusion through defects in a 1 nm Ru thin film.³⁰ While the Cu-Ru system has a large positive heat of formation, He et al. showed simulations and results that indicated a range of metastable amorphous Cu-Ru alloys.³¹ Alonso and de Tendler proposed that the formation of a Cu-Ru amorphous alloy arises from the mutual frustration between the fcc and hcp solid solutions.³² In our XPS scans, Ru 3d core levels after annealing are unchanged suggesting that the formation of a Cu-Ru layer did not occur or was localized to a few layers at the interface. Overall, the Cu on a Ru adhesion layer exhibits thermal stability for annealing up to 400 °C.

IV. CONCLUSION

Different Cu/(Ti, Pt or Ru)/Ta multilayer structures have been prepared by e-beam evaporation and characterized with XPS, AFM, and RBS. The Ta RBS peaks remain unchanged after annealing, indicating negligible diffusion at the Ta interfaces. The stability of these interfaces is crucial to providing a diffusion barrier layer and a smooth substrate for Cu deposition.

For Cu/Ti/Ta system, both the XPS and RBS spectra indicate Ti accumulated on the surface after 400 °C annealing. In the Cu/Pt/Ta system, Pt interdiffusion was detected from both XPS and RBS. In comparison, it appears Ti diffused into Cu to a greater degree than Pt into Cu. The interdiffusion could be described by the Kirkendall effect. Ru as an adhesion layer exhibits a stable interface with Cu after 400 °C annealing. All the surfaces were relatively smooth after annealing excluding islanding or dewetting.

In this study, we suggest that a bilayer structure of 4 nm of Ta and 7 nm of Ru will serve as a diffusion barrier and direct plate layer for Cu electrodeposition. Combined with our previous results which reported a plasma cleaning process for removal of the Ru native oxide, it appears that this Ru/Ta bilayer could replace the current PVD-Cu/Ta barrier layer for Cu interconnects.

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