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Morphology and Thermal Stability of Me-Si-N (Me=Re, W, Ta) for Microelectronics

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Abstract : Low pressure chemical vapor deposition (LPCVD) of Me-Si-N (Me= Re, W, Ta) thin films were investigated for use as diffusion barrier between Cu overlayer and oxidized silicon substrates. Their "amorphous" or nanocrystalline structure is expected to provide better performance than usual polycrystalline barriers. For the CVD process, gaseous precursors were silane, in situ fabricated metal chloride, ammonia, hydrogen and argon. Preliminary thermodynamic simulations of the Me-Si-N and the CVD Me-Si-N-Cl-H-Ar systems (Me=Re, W, Ta), were combined to the experimental study. The Re-Si-N and W-Si-N layers crystallization temperature was found to be around 1173 K after annealing in vacuum by Rapid Thermal Annealing. Their morphology, thermal stability and resistivity were evaluated as a function of annealing temperature.

1. INTRODUCTION

Amorphous ternary barriers against copper diffusion into silicon or SiO₂ are now being investigated as an attractive alternative to polycrystalline counterparts. These new materials are usually composed of one metal, one non metal (Si or B) component and nitrogen such as Ta-Si-N [1-3], W-Si-N [4], W-B-N [5], Ti-Si-N [6,7]. Most of them were elaborated by Physical Vapor Deposition (PVD) and they were particularly studied for applications in microelectronics. Their very high crystallization temperature (around 1173 K) is one of remarkable properties. Indeed, the lack of grain boundaries provides these materials with very good performance as diffusion barrier. For instance, different works showed that PVD Ti-Si-N barrier did not fail until 923 K [6] or 1123 K [7], PVD W-Si-N until 1073 K [4], and PVD Ta-Si-N until 1123 K[1-3].

The objective of this work is to compare the morphology and thermal stability (in terms of crystallization temperature and nature of the crystallized phases) of Me-Si-N (Me= Re, Ta, W) thin films and establish a relationship between the stability of metal nitride Me-N and the Me-Si-N thermal behavior. Low Pressure Chemical Vapor Deposition (LPCVD) technique was chosen since it is more and more attractive for

submicron devices because of good step coverage and possible selectivity.

In this paper, the thermodynamic and experimental results for Re-Si-N are presented. The study on the Ta-Si-N and W-Si-N systems is now going on and preliminary results are reported.

For the elaboration of ternary alloys, gaseous precursors were : in situ fabricated metal chloride, silane and ammonia, diluted in hydrogen and argon.

X-Ray Diffraction analysis was performed using a $\theta/2\theta$ detector with a fine monochromated Fe-K α beam, on as-deposited and annealed films. The films were observed by Transmission and Scanning Electron Microscopy (TEM and SEM), and their composition was determined by Rutherford Backscattering spectroscopy (RBS). Finally, the resistivity and the properties of LPCVD $\text{Me}_x\text{Si}_y\text{N}_z$ (Me= Re, W) films are compared with films obtained with physical methods.

2. THERMODYNAMICS

The thermodynamic simulation, based on the minimization of the Gibbs free energy of the total Me-Si-N-H-Cl-Ar systems (Me= Re, W, Ta), was performed with Melange software [8] to provide the ternary phase diagrams and the nature of the phases present at equilibrium under the experimental chlorination and deposition conditions. Most of the data on the species generated in these systems came from the Scientific Group Thermodata Europe (SGTE) bank [9]. For the species not covered by this data bank, the data were critically selected from the literature available, particularly the data for rhenium silicides were taken from the work of J.S. Chen et al. [10], for the $\beta\text{-Si}_3\text{N}_4$ from the work of P. Rocabois [11]. The data for metal chlorides and silicides came from the studies of LPCVD ReSi_2 [12], WSi_2 [13] and TaSi_2 [14]. Data for the metal nitrides TaN and Ta_2N were taken from Barin & Knacke compilation [15]. To our knowledge, no Re-N compound has been reported. In the case of W-N, there is very little experimental information. Some uncertainties on the existence at elevated temperatures (above 550 K) of different nitrides were found in the literature [16-17]. Only one author proposed a complete calculated thermodynamic phase diagram [18]. First, we considered that in our investigated temperature (above 700 K) and pressures (from 133 to 10^5 Pa) ranges, there are no stable tungsten nitrides. The ternary phase diagram W-Si-N established at 1000 K looks like the Re-Si-N diagram with three equilibria between Si_3N_4 and Me, Me_5Si_3 , MeSi_2 (Me=W, Re). In the three Me-Si-N systems, as no ternary phase was reported in the literature, we assumed that no ternary phases exist. Similarly, we did not consider a thermodynamic description of any amorphous phases, even though amorphous films are expected to be deposited. We assumed that an amorphous material can be simulated as a mixture of crystalline compounds, for the same ternary composition. Ternary phase diagrams Re-Si-N (fig.1) and Ta-Si-N (fig.2) were calculated at different temperatures and pressures. On the other hand, the Ta-Si-N one is really different, with various equilibria: there is no Si_3N_4 -Ta equilibrium, the tantalum silicides are in equilibrium with TaN. On figure 2 is drawn the experimental domain of several studies of E. Kolawa et al. [1-3] who elaborated "amorphous" PVD $\text{Ta}_{0.36}\text{Si}_{0.14}\text{N}_{0.50}$ films.

The thermodynamic simulation of rhenium, tungsten and tantalum chlorinations were carried out for the elaboration of ReSi_2 [12] WSi_2 [13] and TaSi_2 [14] thin films, respectively.

Figure 1: Ternary phase diagram Re-Si-N at 1073 K with simulated conditions (dot B, C, D) and experimental compositions ("amorphous zone").

Figure 2: Ternary phase diagram Ta-Si-N established at 800 K with E. Kolawa et al. [1-3] experimental domain.

The experimental rhenium and tantalum chlorination temperature and the total pressure were fixed to 823 K and to $1.197 \cdot 10^3$ Pa (9 Torr). For tungsten chlorination, temperature and pressure were 1023 K and $0.665 \cdot 10^3$ Pa (5 Torr), respectively. According to the thermodynamic results, for the above-mentioned experimental conditions, gaseous precursors ReCl_5 (g), WCl_4 (g), and TaCl_4 (g)+ TaCl_5 (g) were expected to be fabricated and transported [12-14]. In the case of the tungsten chlorination, this result was confirmed with a mass spectrometric investigation [13].

For the Re-Si-N system (fig.1), various phases could be obtained, but three different experimental points labeled B, C, D, which have been previously described [19], were retained. They correspond to the 3 domains : $\text{Re} + \text{Re}_5\text{Si}_3 + \text{Si}_3\text{N}_4$ (dot B), $\text{Re}_5\text{Si}_3 + \text{Si}_3\text{N}_4$ (dot C), $\text{Re}_5\text{Si}_3 + \text{Si}_3\text{N}_4 + \text{ReSi}_2$ (dot D). For the elaboration of W-Si-N, the tested experimental condition was simulated in the $\text{W} + \text{Si}_3\text{N}_4 + \text{N}_2$ (g) domain.

3. EXPERIMENTAL

In this paper, only results on Re-Si-N and W-Si-N films are presented. Ternary Me-Si-N films were elaborated in a vertical cold wall low pressure reactor described elsewhere [20]. The rhenium and tungsten chloride gaseous precursors were processed by in situ chlorination in the top section of the reactor. Rhenium pellets or tungsten wires were set up in a quartz tube and heated by a lamp furnace at respectively 823 K and 1073 K, whereas chlorine passed through and formed ReCl_5 (g) or WCl_4 (g) [12-13]. Prior to deposition, the chlorination chamber was regenerated by heating the metallic charge at 823 K (Re) and 1073 K (W) in a hydrogen reducing atmosphere during 15 to 30 minutes. This procedure was carried out to remove metal oxides and oxychlorides which may be present on the metal surface.

Layers were deposited on thermally oxidized <100> oriented silicon (100nm SiO_2 thickness). Deposition process was carried out at 1073 K for rhenium and 773 K for tungsten under a total pressure of $1.197 \cdot 10^3$ Pa (9 Torr) and $0.665 \cdot 10^3$ Pa (5 Torr), respectively. For the Re-Si-N and W-Si-N deposition, chlorine flow rate was fixed to 5 and 4 sccm/min, hydrogen to 90 and 200 sccm/min, diluted silane to 650 and 500 sccm/min, respectively. Ammonia flow rate was varying from 2 to 10 sccm/min for Re-Si-N and was fixed to 30 sccm/min for W-Si-N, in an argon atmosphere for a total flow rate of 1l/min. The as-deposited films were annealed in vacuum for 1 minute between 873 and 1273 K by rapid thermal annealing (RTA) in vacuum ($6.65 \cdot 10^{-2}$ Pa).

4. RESULTS AND DISCUSSION

X-Ray diffraction on as-deposited Re-Si-N films showed a nanocrystalline or amorphous morphology without any defined diffraction peak (curve a, fig. 3), whatever deposition conditions and substrate. After RTA in vacuum at 1173 K, there was a Re crystallization in all the films (curve b). In the same way, there was a metal crystallization for tungsten (fig. 4).

In the case of PVD Ta-Si-N films, J.S. Reid et al.[4] mentioned that under vacuum annealing, the $\text{Ta}_{0.36}\text{Si}_{0.14}\text{N}_{0.50}$ films crystallized at 1373 K into Ta_2N , Ta_5Si_3 and " $\text{Ta}_{4.5}\text{Si}$ " and did not liberate nitrogen.

For the three tested conditions, RBS analysis gives an average composition of $\text{Re}_{0.26}\text{Si}_{0.34}\text{N}_{0.40}$ (located in the "amorphous zone" in fig. 1). Films may be composed with a mixture of 1/4 Re+3/4 non

crystallized " Si_3N_4 ", with an excess of Si for all the selected points. After annealing, the overall composition did not change and no nitrogen out-gazing was evidenced under the uncertainties of RBS.

Transmission Electronic Microscopy (TEM) observation (fig. 5.a) showed on as-deposited Re-Si-N layer deposited on Si/SiO₂ (1000 Å), that the ternary alloy appeared as a composite of very small particles identified as Re inserted in a non-crystallized " Si_3N_4 " matrix.

Figure 3: X-Ray Diffraction ($\theta/2\theta$ scan detector mode, Fe- $K\alpha$) spectra on: as-deposited Re-Si-N film (a), and annealed film in vacuum at 1173 K (b).

Figure 4: X-Ray Diffraction ($\theta/2\theta$ standard mod, Fe- $K\alpha$) spectra on: as-deposited W-Si-N film (a), film annealed in vacuum at 1173 K (b)

The average Re grain size was measured approximately to 15 Å. As revealed in fig.5.b, RTA at 1073 K in vacuum lead to grain growth since the average grain size reached then 50 Å. The material was now composed by spherical Re grains inserted in non-crystallized Si₃N₄ (that will not crystallize until 1700 K [21]).

Figure 5 : TEM pictures on cross-section of as-deposited Re-Si-N/SiO₂/Si (a), and ReSi-N/SiO₂/Si after RT Annealing at 1073 K

Resistivity was measured on as-deposited and annealed Re-Si-N (table 1) and W-Si-N films by the four point probes technique at room temperature. The resistivity of CVD Re-Si-N films increased with annealing temperature from 15 to 31 mΩcm at 1073 K and after annealing at 1173 K measurement was not possible any more. Two explanations could be proposed:

- an oxidation occurring with the annealing
- the increase of the distance between the rhenium particles (conductive phase) scattered in Si_3N_4 (dielectric phase)

	Re-Si-N film resistivity ($\text{m}\Omega\text{cm}$)
as-deposited	15
annealed at 873 K	28
annealed at 1073 K	31
annealed at 1173 K	-

Table 1: Resistivity of Re-Si-N films as a function of their thermal treatments.

The CVD W-Si-N layer resistivity value was found to be around $1.4 \text{ m}\Omega\text{cm}$ which is comparable to the obtained value ($1.8 \text{ m}\Omega\text{cm}$) on PVD W-Si-N films [4]. The PVD Ta-Si-N thin films [1-3] resistivity was measured to $0.625 \text{ m}\Omega\text{cm}$.

To check the step coverage of LPCVD Me-Si-N layers, a Re-Si-N film was deposited on patterned substrate and was observed by SEM. Figure 6 represents a cross-section micrograph of the Re-Si-N film on SiO_2 steps, and shows a step coverage ratio around 1. That confirms that this CVD process is a promising technique for submicron devices.

Figure 6 : Cross-section of a Re-Si-N film deposited over a patterned SiO_2 substrate.

5. CONCLUSION

Morphology and thermal stability of ternary Me-Si-N thin films (Re, W, Ta), were investigated.

LPCVD Re-Si-N films, deposited on SiO_2 at 1073 K, were found to be composed of Re grains inserted in a non-crystallized Si_3N_4 matrix. Annealing lead to Re grain growth and Re peaks were observed after annealing at 1073 K by X-Ray Diffraction. The first results on W-Si-N system indicated that it crystallized at 1173 K in the metal phase (W) such as the Re-Si-N system. PVD Ta-Si-N thin films fabricated by E.

Kolawa et al. [1-3] and J.S. Reid et al. [4] crystallized in tantalum silicides and tantalum nitrides at 1373 K. The existence or non-existence of stable metal nitride could explain the differences observed in morphology and resistivity of these three systems.

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