

Interface Reaction of SiO₂/ Ta and Its Influence on Cu Diffusion *

Long Shibing¹, Ma Jidong¹, Yu Guanghua¹, Zhao Hongchen¹, Zhu Fengwu¹,
Zhang Guohai² and Xia Yang²

(1 Department of Materials Physics, Beijing University of Science and Technology, Beijing 100083, China)
(2 Microelectronic Research & Development Center, The Chinese Academy of Sciences, Beijing 100029, China)

Abstract : Ta/ NiFe film is deposited on Si substrate precoated with SiO₂ by magnetron sputtering. SiO₂/ Ta interface and Ta₅Si₃ standard sample are investigated by using X-ray photoelectron spectroscopy (XPS) and peak decomposition technique. The results show that there is a thermodynamically favorable reaction at the SiO₂/ Ta interface : $37\text{Ta} + 15\text{SiO}_2 = 5\text{Ta}_5\text{Si}_3 + 6\text{Ta}_2\text{O}_5$. The more stable products Ta₅Si₃ and Ta₂O₅ may be beneficial to stop the diffusion of Cu into SiO₂.

Key words : copper interconnection in ULSI; diffusion barrier; interface reaction; X-ray photoelectron spectroscopy

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1 Introduction

As the electrical resistivity of copper ($1.7\mu\Omega\cdot\text{cm}$) is far lower than that of aluminum ($2.7\mu\Omega\cdot\text{cm}$), the replacement of Al and its alloys by Cu as the interconnections of Ultra-Large Scale Integration (ULSI) devices can greatly decrease the RC time delay of circuits. Thus, their performances such as speed, power dissipation, integration density, etc., can be greatly improved^[1~3]. In addition, when the texture of Cu is (111), the electromigration resistance of Cu wires will improve two orders of magnitude compared with that of conventional Al interconnections, and there will be no interconnection vacancy resulting from stress migration^[2~4]. In consequence, the reliability of circuits can be enhanced.

However, Cu is a fast diffuser in SiO₂ and Si^[5]. Furthermore, Cu is a kind of bad dopant in Si. When Cu dif-

fuses into Si, it will form several deep acceptor levels within the forbidden band gap of Si. These levels will act as generation-recombination centers or traps and alter the density and life of the non-equilibrium minor carriers^[6]. In addition, Cu and Si will also form Cu₃Si precipitate with high electrical resistivity at temperatures as low as 200 °C^[4], as a result of which leakage currents will generate through shallow source and drain junctions^[7]. Hence a barrier layer between Cu and dielectric materials such as SiO₂ is crucial to block the diffusion of Cu.

Tantalum is a promising barrier material. First of all, Ta is immiscible with Cu^[8] and the Cu-Ta system is expected to be very stable at high temperatures^[4,9], so Ta can sufficiently block the diffusion of Cu. Clevenger *et al.* showed that a 20-nm-thick Ta film annealed in nitrogen prevents Cu from diffusion up to 630 °C^[5,9]. On the other hand, the sputter-deposited Ta is metastable tetragonal -

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Long Shibing male, was born in 1977, MS candidate. He is engaged in the research on copper interconnection technology in ULSI.

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Ta. While -Ta sputtered on SiO₂ has a strong texture with its closest packed plane (002) parallel to the film surface. Subsequently, the growth of (111) Cu is preferred, which has superior electromigration resistance^[4,11].

Although much research has been made on Ta and Cu, the microscopic mechanism for Ta to block Cu diffusion has not been very clear. At the same time, interface reactions between different materials especially different films alter the local structure and chemistry, and consequently the physical properties. This field of research is therefore important both scientifically and technologically. New stable or metastable phases will form near the interfaces and make the interfaces more stably due to interface reactions. As for the interface between Ta and Cu, Kwon *et al.*^[11] have investigated elaborately. But no research has been reported about the interface between Ta and SiO₂. In this paper, Ta/NiFe film was deposited onto (100) single crystal Si substrate precoated with 300-nm-thick SiO₂ by magnetron sputtering. And we investigated the interface between SiO₂ and the as-deposited Ta using XPS. It is found that there is a thermodynamically favorable chemical reaction at the SiO₂/ Ta interface and the products may be beneficial to stop the diffusion of Cu into SiO₂ in copper interconnect in ULSI.

2 Experimental

The samples for XPS analyses were: (1) Ta₅Si₃ powder with purity of 99.5%, provided by Alfa Aesar Company in USA, as the standard sample for XPS spectrum; (2) the sample including SiO₂/ Ta interface, prepared in DV-502 magnetron sputtering system: about 5-nm-thick Ta film was first deposited by DC sputtering at room temperature onto 300-nm-thick SiO₂ thermally grown on (100) single crystal Si substrate. Then a 10-nm-thick NiFe film was deposited without vacuum breaking onto Ta to protect the Ta layer from the oxidation after the sample was taken out of the vacuum chamber. The base pressure of sputtering chamber was less than 4×10^{-5} Pa and the Ar sputtering pressure was 0.5 Pa. The substrates were cooled by

water.

The samples were introduced into a MICROLAB MK X-ray photoelectron spectroscopy system instantly after being taken out of the deposition system. A Mg K line at 1253.6 eV was used. The vacuum of the analysis chamber was less than 3×10^{-7} Pa. The scanning mode of energy analyzer was CAE and its pass energy was 50 eV. In order to detect the composition and chemical states at the SiO₂/ Ta interface using XPS, the SiO₂/ Ta interfacial layer has to be within the XPS detectable sampling depth $d = 3 \lambda \sin \theta$ ^[12], where λ and θ represent inelastic mean-free paths (IMFPs) for photoelectrons and a take-off angle for photoelectrons with respect to the samples surface plane, respectively. About 95% of the total photoelectron signals will arise from this sampling depth. The IMFPs can be obtained from the table compiled by Liu *et al.*^[13]. For a Mg K radiation source, the IMFPs for Si2p in Si and Ta4f in Ta are 2.2 nm and 1.9 nm respectively. When $\theta = 90^\circ$, the detectable depth $d = 3 \lambda$. In order to obtain the signal from the SiO₂/ Ta interface, the samples were sputtered by lower energy Ar⁺ to remove the whole NiFe layer and a certain thickness of Ta layer until the Ta⁵⁺ 4f peak appeared. The sputter rate of Ar⁺ to Ta layer had been accurately calibrated. The Ar⁺ gun was operated at 500 V at a pressure of 1×10^{-4} Pa and the Ar⁺ current intensity was 50 μ A/cm². To eliminate the influence of static electricity accumulation effect, the binding energy of each XPS spectrum was calibrated by C1s peak and 284.6 eV was adopted as the standard C1s binding energy. The XPS peak areas and peak decomposition (i. e. "curve fitting") were determined using Guassian (80%)-Lorentzian (20%) curves fitting software (including the atomic sensitivity factor) provided by the XPS system. Peak areas were measured with a precision of 5% or better.

3 Results and discussion

Figure 1 shows the Si2p high resolution spectrum near the SiO₂/ Ta interface for $\theta = 90^\circ$. The binding energy of the Si2p photoelectron peak is 102.50 eV, which is

neither the peak of pure Si (99.1eV), nor that of Si^{4+} in SiO_2 (103.3eV)^[14]. Ta_5Si_3 powder with purity of 99.5%, provided by Alfa Aesar Company in USA, was analyzed by XPS. As shown in Fig. 2, its Si2p photoelectron peak locates at 102.35eV. These results show that within the experimental error, the position of Si2p peak near the SiO_2/Ta interface (as shown in Fig. 1) is the same as that of Si2p peak of Ta_5Si_3 (as shown in Fig. 2). Consequently, from the chemical state of Si, we believe that there is Ta_5Si_3 product near the SiO_2/Ta interface when Ta is sputtered onto SiO_2 .

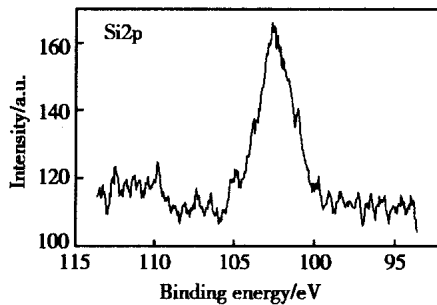


Fig. 1 Si2p XPS spectrum obtained near SiO_2/Ta interface for $\theta = 90^\circ$

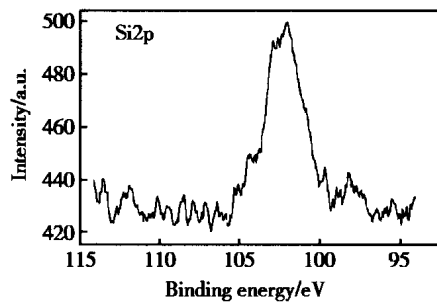


Fig. 2 Si2p XPS spectrum of Ta_5Si_3 standard sample for $\theta = 90^\circ$

Figure 3 represents a computer fitting curve of a Ta4f high-resolution XPS spectrum obtained near the SiO_2/Ta interface for $\theta = 90^\circ$, and it can actually be fitted with four components. From the XPS handbook^[14], we know that peak 1 at 21.7eV is a characteristic of a metallic Ta4f_{7/2} peak, and peak 2 at 23.5eV represents Ta4f_{5/2} peak; peak 3 at 26.2eV corresponds to Ta4f_{7/2} peaks of

Ta_5Si_3 and Ta_2O_5 (their standard Ta4f_{7/2} peak positions are at 26.5eV and 26.3eV respectively) and peak 4 at 28.1eV corresponds to their Ta4f_{5/2} peaks. So, from the chemical state of Ta, we believe that there are Ta_5Si_3 and Ta_2O_5 products at the SiO_2/Ta interface.

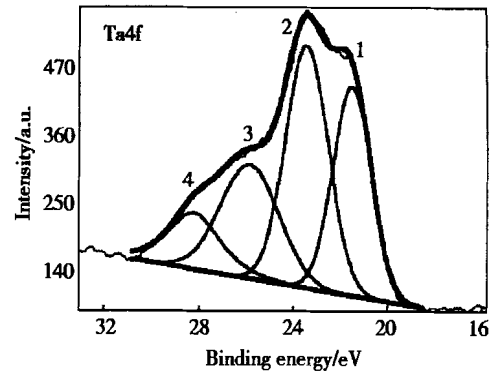


Fig. 3 Computer fitting curve of Ta4f high-resolution XPS spectrum obtained near SiO_2/Ta interface for $\theta = 90^\circ$

The results of XPS indicate that there is a "intermixing layer" near the SiO_2/Ta interface which is made up of Ta, Ta_5Si_3 and Ta_2O_5 , etc. The existence of Ta_5Si_3 and Ta_2O_5 near the SiO_2/Ta interface can be understood by considering the reaction: $37\text{Ta} + 15\text{SiO}_2 = 5\text{Ta}_5\text{Si}_3 + 6\text{Ta}_2\text{O}_5$. From the thermodynamics data presented by literature^[15], we calculated the Gibbs free energy change of this reaction. The value is about -319.42kJ/mol , which means that the reaction is thermodynamically favorable. On the other hand, the formation enthalpy H of SiO_2 is 9.46eV ^[16]. The atoms which had been sputtered off from the target and arrived at the substrate were provided with kinetic energy of about several to more than tens eV^[17]. Therefore the reaction is dynamically possible. As the results of this reaction, new compound phases, Ta_5Si_3 and Ta_2O_5 form at the interface, which make the interface more stably. Since Ta_5Si_3 and Ta_2O_5 are more stable and have more complicated crystal structure than pure Ta, it is expected that the diffusion of Cu in them is more difficult than that of Ta. That is to say, if Cu has diffused into Ta, Ta_5Si_3 and Ta_2O_5 could block the further diffusion of Cu

into SiO₂ and even Si to some extent. In consequence, the interface reaction between Ta and SiO₂ may be beneficial to stop the diffusion of Cu into SiO₂ in copper interconnections of ULSI when Ta is taken as a diffusion barrier.

4 Conclusion

In view of the XPS analysis of SiO₂/ Ta interface, we report the evidence of chemical reaction which takes place at SiO₂/ Ta interface: $37\text{Ta} + 15\text{SiO}_2 = 5\text{Ta}_5\text{Si}_3 + 6\text{Ta}_2\text{O}_5$. The more stable new compounds, Ta₅Si₃ and Ta₂O₅, formed at the SiO₂/ Ta interface, may be beneficial to block the diffusion of Cu into SiO₂ in Cu interconnections of ULSI when Ta is taken as a diffusion barrier.

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SiO₂/ Ta 界面反应及其对铜扩散的影响*

龙世兵¹ 马纪东¹ 于广华¹ 赵洪辰¹ 朱逢吾¹ 张国海² 夏 洋²

(1 北京科技大学材料物理系,北京 100083)

(2 中国科学院微电子中心,北京 100029)

摘要: 利用磁控溅射方法在表面有 SiO₂ 层的 Si 基片上溅射 Ta/NiFe 薄膜,采用 X 射线光电子能谱 (XPS) 研究了 SiO₂/ Ta 界面以及 Ta₅Si₃ 标准样品,并进行计算机谱图拟合分析.实验结果表明在制备态下在 SiO₂/ Ta 界面处发生了热力学上有利的化学反应: $37\text{Ta} + 15\text{SiO}_2 = 5\text{Ta}_5\text{Si}_3 + 6\text{Ta}_2\text{O}_5$,界面处形成更稳定的化合物新相 Ta₅Si₃、Ta₂O₅.在采用 Ta 作阻挡层的 ULSI 铜互连结构中这些反应产物可能有利于对 Cu 扩散的阻挡.

关键词: ULSI 铜互连; 扩散阻挡层; 界面反应; X 射线光电子能谱

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龙世兵 男,1977 年出生,硕士研究生,主要从事超大规模集成电路铜互连线技术研究.

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