

Characterization of Surface Oxides in Gold Thin Films with V- and Ti- underlays by AES and XPS

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(Received November 20, 1991)

AES/XPS를 이용한 Au/V, Au/Ti 박막의 표면산화물 분석

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(1991년 11월 20일 접수)

Abstract—Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) analyses have been performed on double-structured Au/V and Au/Ti thin films after heat treatment at 500°C in air. V- and Ti-underlays sandwiched between gold thin films and SiO₂ substrates form oxides on the free surface of gold films during the heat treatment. The chemical compositions of the oxides were identified as V₂O₅ and TiO₂ in Au/V and Au/Ti thin films, respectively.

요약—Au/V, Au/Ti의 이중구조 박막을 대기 중에서 500°C에서 열처리한 후 Auger electron spectroscopy(AES)와 X-ray photoelectron spectroscopy(XPS)를 이용하여 분석하였다. 열처리 과정에서 Au와 SiO₂ 기판 사이의 V-와 Ti- 하층박막은 Au 표면 위에 산화물을 형성하였다. 산화물의 화학조성은 Au/V, Au/Ti 박막에서 V₂O₅와 TiO₂로 각각 판명되었다.

1. Introduction

In gold metallizations, a metal underlay is required to provide good bonding to the substrate because gold does not readily adhere to oxide or oxidized substrates commonly used for microelectronic circuits and tends to ball up during heat treatment even below the melting point[1-2].

V and Ti have been widely used for a diffusion barrier between metallization and devices. Also they have been known to improve the bondability to the substrate. However, these underlays diffuse out and form oxides on the free surface and along the grain boundary, which may affect the stability of thin film metallizations[2].

This study presents the formation of surface ox-

ides formed in Au/V and Au/Ti films during heat treatments, and their characterizations.

AES and XPS were employed to determine the chemical composition of the film surface and throughout the film thickness.

2. Experimental Procedure

A titanium (or vanadium) film of 130 Å thickness was sandwiched between quartz substrates and gold films of about 750 Å thickness by successive thermal evaporation from W boats (Ti and V) or Mo boats (Au) in a high vacuum in the 10⁻⁷ Torr range without breaking the vacuum. The deposition rates ranged from 4 to 8 Å/s. This configuration will be hereafter called "Au/Ti or Au/V composite"

film.

Isothermal heat treatment was carried out in a quartz tube furnace at 500°C for 1 hour in air. Following heat treatment, the chemical composition of the film surface was characterized using Auger electron spectroscopy (AES). Auger sputter profiling was used to examine the atomic species contained throughout the thickness of the films. Depth-composition profiles were made by argon sputtering. The critical conditions for the analysis were as follows: electron gun beam voltage: 10 KV; electron gun beam current: 0.01 μ A; electron multiplier voltage: 1600 V; base pressure: $<1 \times 10^{-9}$ Torr; pressure during Ar ion sputtering: 3×10^{-8} Torr; ion gun voltage: 3 KV; ion gun emission current: 25 mA; raster size: 3×3 (mm²). Auger transitions of V LMM, Ti LMM, O KLL and Au NVV were used for the measurement of the peak-to-peak amplitude.

The chemical states of metal oxides formed during isothermal heat treatment were characterized by X-ray photoelectron spectroscopy (XPS). The XPS data were obtained using Mg K α radiation and operating the hemispherical analyzer at the medium resolution with a fixed retarding ratio (F. R. R.) scan mode, in which the area of sample analyzed remains constant throughout the whole kinetic energy range. The position of C 1s peaks were measured and moved at 284.6 eV[3].

3. Results and Discussion

3.1. Au/V composite films

In order to identify the chemical state of vanadium underlays in as-deposited Au/V composite films, AES spectra were taken after sputter etching. Fig. 1(a) and 1(b) show Auger spectra taken from a vanadium underlay after 9.9 min. and 10.5 min. Ar sputtering, respectively. The kinetic energies of the V LMM peaks at 431.5 and 437.5 eV have features of metallic vanadium[4].

Vanadium underlays form vanadium oxide during heat treatment in air. To investigate the chemical state of the vanadium oxide, an XPS analysis was performed on a heat treated Au/V composite film. Fig. 2 depicts XPS spectra of the V 2P peaks taken from the surface of an Au/V composite film

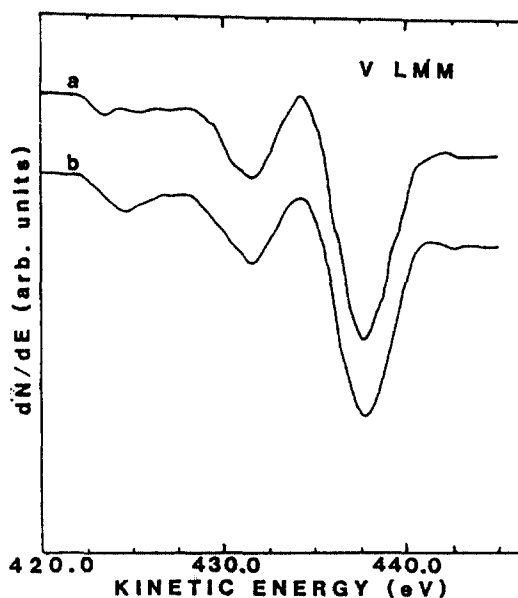


Fig. 1. AES spectra taken from an as-deposited Au/V composite film.

- (a) vanadium underlay after 9.9 min. sputtering.
- (b) vanadium underlay after 10.5 min. sputtering.

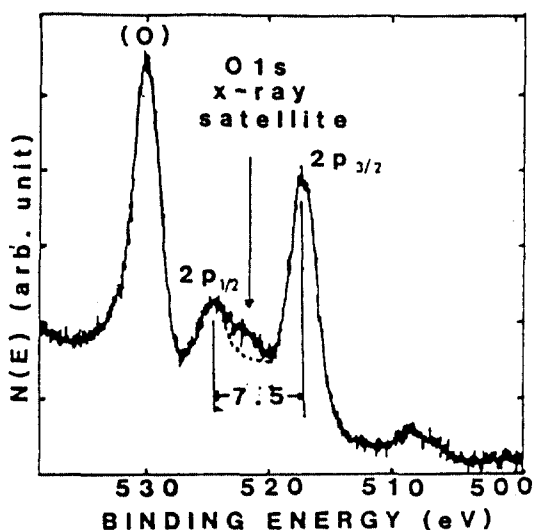


Fig. 2. XPS spectrum of the vanadium 2P peaks taken from the surface of an Au/V composite film heat treated at 500°C in air.

heat treated at 500°C. Binding energies for the V2P_{1/2} and 2P_{3/2} peaks were located at 524.9 eV and

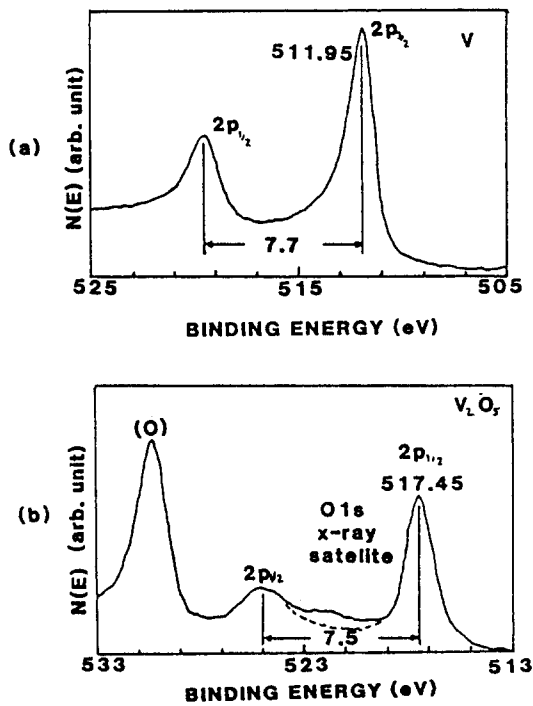


Fig. 3. XPS spectra of (a) metallic V and (b) V_2O_5 [from ref. 3].

517.4 eV, respectively. These binding energies and the energy separation of 7.5 eV between the two V 2P peaks correspond to those of V_2O_5 [3]. The O 1s X-ray satellite is seen between the two V 2P peaks as marked in Fig. 2. Fig. 3 illustrates XPS spectra taken from the XPS handbook[3] of the V 2P peaks of the metallic V (Fig. 3(a)) and those of V_2O_5 (Fig. 3(b)). The differences in XPS spectra between metallic V and V_2O_5 are evident.

The information depth of XPS is about 10-30 Å caused by the escape depth of the electrons[5]. Thus the vanadium underlays cause vanadium oxide to form on the free surface of gold films during heat treatment in air. Its chemical state was identified as V_2O_5 in the XPS spectra.

In order to study the change of the chemical state of vanadium throughout the film thickness, a series of AES spectra were taken at various sputtering times. Fig. 4 shows a series of Auger spectra taken from an Au/V composite film heat treated at 500°C.

The top four AES spectra were taken from the

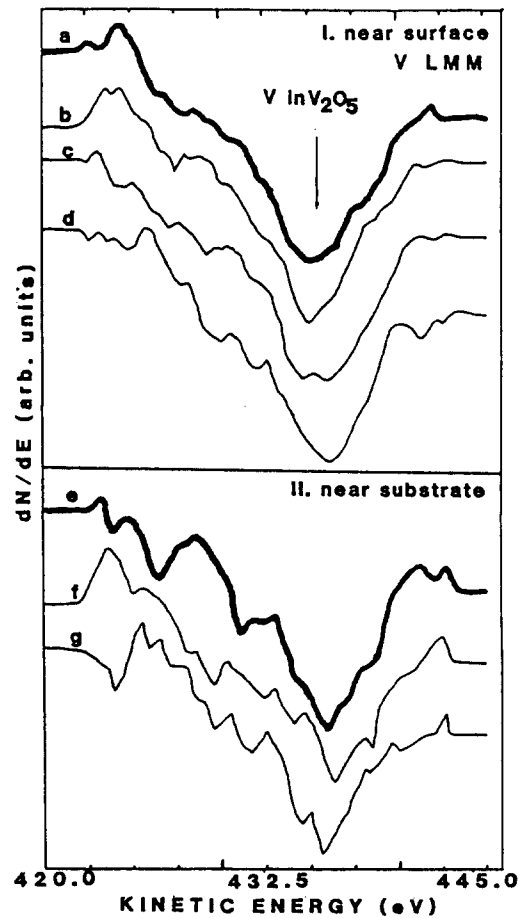


Fig. 4. AES spectra, dN/dE , taken from an Au/V composite film heat treated at 500°C in air.

I. near surface :

- (a) before sputtering.
- (b) after 0.3 min. sputtering.
- (c) after 0.9 min. sputtering.
- (d) after 1.5 min. sputtering.

II. near substrate :

- (e) after 16.5 min. sputtering.
- (f) after 17.1 min. sputtering.
- (g) after 17.7 min. sputtering.

surface region of the film, i.e., on the surface (Fig. 4 (a)), after 0.3 (Fig. 4(b)), 0.9 (Fig. 4(c)) and 1.5 (Fig. 4 (d)) min. sputtering. The bottom three AES spectra were taken from the vanadium underlay region near the substrate, i.e., after 16.5 (Fig. 4(e)), 17.5 (Fig. 4(f)), and 17.7 (Fig. 4(g)) min. sputtering. It is seen in Fig. 4 that the kinetic energy of the V LMM peaks appears at about 436 eV throughout the film

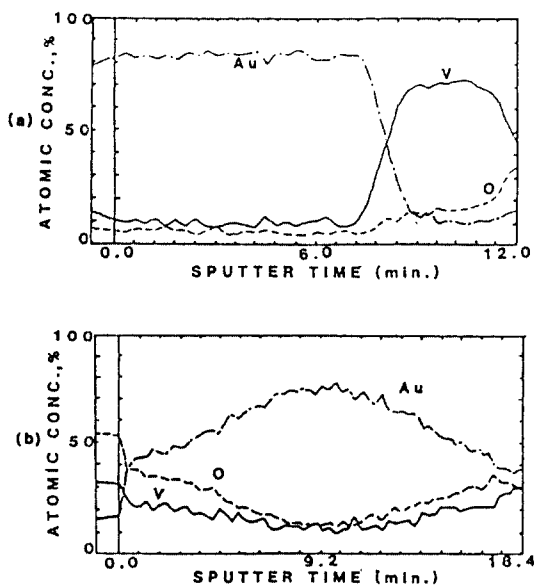


Fig. 5. Auger sputter profiles of Au/V composite films. (a) as-deposited. (b) heat treated at 500°C.

of the heat treated Au/V composite film. As mentioned above, the chemical state of vanadium oxide formed during heat treatment in air is V_2O_5 . Thus the Auger spectra in Fig. 4 are believed to be due to the formation of vanadium oxide (V_2O_5) throughout the film.

In the case of vanadium, it has been reported that vanadium forms V_3Si with the SiO_2 substrate during heat treatment under vacuum at about 800°C for 3 hours[6]. The vanadium silicide forms towards the substrate side of the metal film, while the metal oxide forms on the free surface. In this study, it was difficult to get Auger informations after exposure of the quartz substrate because of charging effects. It is thus not demonstrated whether the vanadium underlays reacted and formed vanadium silicides with SiO_2 substrate during heat treatment at 500°C in air.

The concentration of vanadium in Au/V composite films was about 5.5 wt.% in this study. Reference to the phase diagram[7] shows that the solubility of V in Au at 500°C is approximately 4.0 wt.%. It is, however, believed by considering the results of XPS in Fig. 2 and the results of AES in Fig. 4 that vanadium underlay mainly forms vanadium

oxide (V_2O_5) during heat treatment in air.

Auger depth profiles were made by argon ion sputtering with computer controlled alternating sputtering and data taking cycles. The resulting profiles are presented in terms of atomic concentration versus sputter etching time in Fig. 5. Auger depth profiles of as-deposited and heat treated Au/V composite films at 500°C are seen. As expected, vanadium is localized near the interface between the gold film and the quartz substrate in an as-deposited Au/V composite film (Fig. 5(a)). High concentration of vanadium and oxygen on the film surface were, however, observed in a heat treated Au/V composite film, which supports the concept of out-diffusion of the vanadium from the underlays and the formation of the vanadium oxide (V_2O_5) on the free surface and in the grain boundaries of gold during heat treatment in air.

3.2. Al/Ti composite film

Fig. 5 shows Auger spectra taken from the titanium underlays after sputter etching. The kinetic energies of the Ti LMM peaks at about 382.5 and 387.5 eV are believed to be those of the metallic tita-

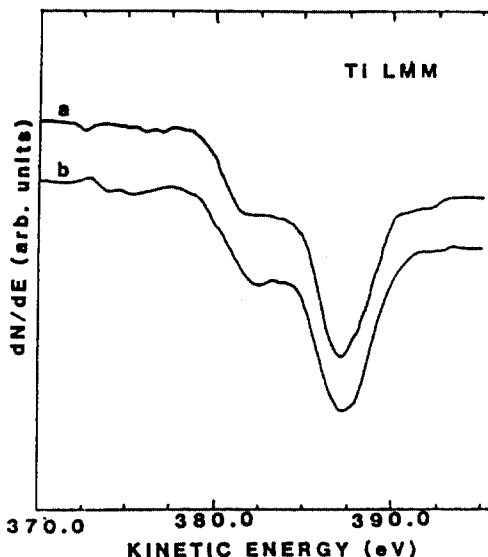


Fig. 6. AES spectra taken from an as-deposited Au/Ti composite film. (a) Titanium underlay after 6.9 min. sputtering. (b) Titanium underlay after 7.5 min. sputtering.

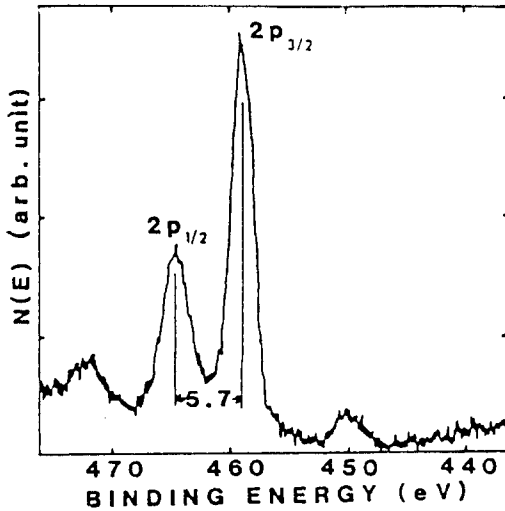


Fig. 7. XPS spectra of the Ti 2p peaks taken from the surface of an Au/Ti composite film heat treated at 500°C.

nium. Compared to 383 and 388 eV for metallic Ti in Auger Hand Book[4], the 0.5 eV difference of kinetic energies for both peaks may result from charging effects. The Ti LMM peaks of TiO_2 appear as one single peak at about 383 eV[8]. The intensity ratios of Ti LMM/LMV transitions can be also used for the determination of chemical states[8].

The titanium underlays cause titanium oxide to form during heat treatment in air. Fig. 7 depicts the XPS spectrum of the Ti 2P peaks taken from the surface of an Au/Ti composite film heat treated at 500°C. Binding energies for the Ti $2P_{1/2}$ and $2P_{3/2}$ peaks were located at 466.6 eV and 458.9 eV, respectively. This binding energies and the energy separation of 5.7 eV between the two Ti 2P peaks correspond to those of TiO_2 [3]. Considering the information depth of XPS, titanium underlays cause titanium oxide (TiO_2) to form on top of gold films during heat treatment in air.

Fig. 8 shows a series of Auger spectra taken from a heat treated Au/Ti composite film. The top four AES spectra were taken from the surface region of the film and the bottom three AES spectra were taken from the titanium underlay region near the substrate. The top four Auger spectra near the film surface are believed to be those of titanium oxide (TiO_2) formed during heat treatment in air. It is,

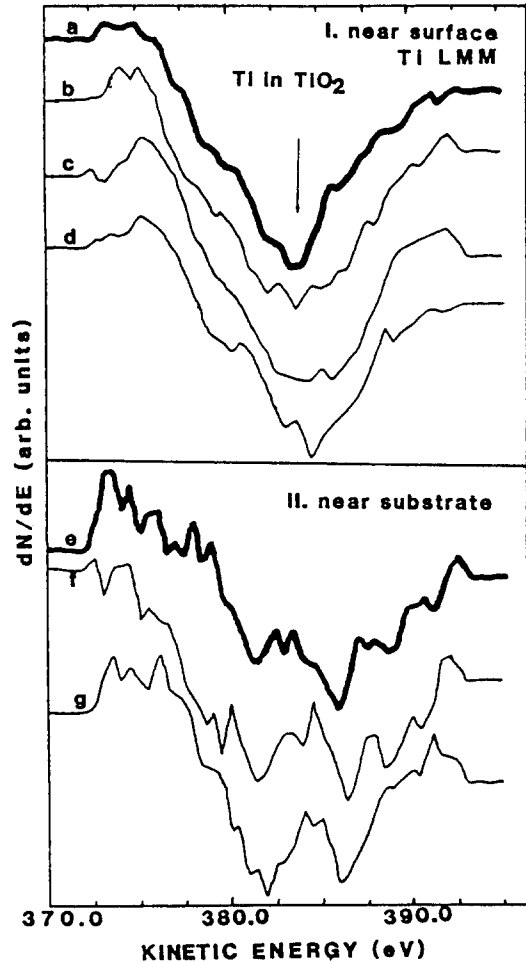


Fig. 8. AES spectra, dN/dE , taken from an Au/Ti composite film heat treated at 500°C.

I. near surface :

- (a) before sputtering.
- (b) after 0.3 min. sputtering.
- (c) after 0.9 min. sputtering.
- (d) after 1.5 min. sputtering.

II. near substrate :

- (e) after 9.9 min. sputtering.
- (f) after 10.5 min. sputtering.
- (g) after 11.1 min. sputtering.

however, not clear whether the two peaks at about 381.5 and 386 eV in Fig. 8(e-g) reveal that titanium underlays react with SiO_2 and form titanium silicide and titanium oxide during heat treatment at 500°C in air because of the high noise level near the quartz substrate.

Titanium has been reported to react with SiO_2

and to form titanium silicide and titanium oxide during heat treatment in cases in which external oxygen is absent (e. g., high vacuum)[6]. This is known due to the negative heat of reaction (ΔH)

V and Ti have been widely used for a diffusion barrier and to improve bondability between metallization and devices. However, V-(and Ti) underlays diffuse out and form oxides on the free surface for this chemical reaction. Thus it is possible that Ti from the underlay might be reacted with the SiO_2 substrate during heat treatment even in air and formed titanium silicide and titanium oxide.

The overall composition of titanium in Au/Ti composite films was about 3.7 wt.% Ti in this study. Reference to the phase diagram[7] shows that the solubility of Ti in Au at 500°C is less than 1.0 wt.%. It is, however, believed that titanium underlays mainly form titanium oxide (TiO_2) on the free surface of gold and along the grain boundaries of gold films during heat treatment in air.

Auger depth-composition profiles are presented in terms of atomic concentration versus sputter etching time in Fig. 9. As expected, titanium is localized near the interface between the gold film and the quartz substrate in the as-deposited Au/Ti composite film (Fig. 9(a)). However, high concentrations of titanium and oxygen on the film surface were observed in a heat treated Au/Ti composite film, which supports the concept of out-diffusion of the titanium from the underlays and the formation of a titanium oxide (TiO_2) on the free surface of gold during heat treatment in air as in the case of Au/V composite films.

4. Conclusion

and along the grain boundaries in Au/V (and Au/Ti) composite films during heat treatment in air. This may affect the stability of thin film metallizations in microelectronic devices. The chemical compositions of the oxides formed during heat treatment in air are V_2O_5 and TiO_2 in Au/V and Au/Ti thin films, respectively.

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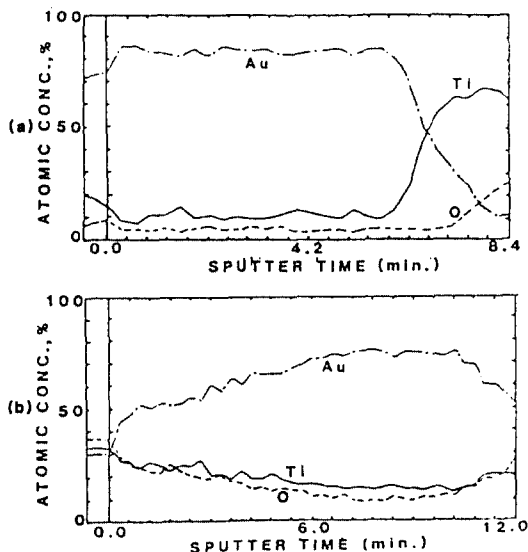


Fig. 9. Auger sputter profiles of Au/Ti composite films.
(a) as-deposited.
(b) heat treated at 500°C .

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