行政院國家科學委員會補助專題研究計畫成果報告

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計畫主持人：李紫原
共同主持人：

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以化學氣相沈積法製作金屬薄膜材料（I）

Preparation of Metal Thin Film Materials by Chemical Vapor Deposition

計畫編號：NSC 89－2113－M－007－29
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一、中文摘要

本計畫將利用低壓化學氣相沈積法，以金屬鹵化物與金屬片為前驅物，在水平熱壁式反應槽中，沈積金屬相關材料於基材上。由於金屬片的置入，可幫助金屬鹵化物還原，在反應槽中即時製作半穩定金屬鹵化物，因此可使沈積反應溫度較僅以金屬鹵化物為前驅物降低許多。

另外鹼金屬與鹼土金屬以及具有強還原能力的還原劑，引入沈積系統中更可和緩反應條件，同時此反應亦可在溶液相進行製作金屬超細微粉末。

關鍵詞：金屬鹵化物，金屬片，鹼金屬，還原劑，金屬細微粉末

Abstract

This work deposited titanium based thin films by a low pressure chemical vapor deposition system on a substrate using a horizontal hot-wall three zone reactor. $TiCl_4$ and a titanium metal plate were used as the precursors to *in situ* prepare TiCln (n=1,2,3) at the first zone with 900℃ reaction temperature. The deposition reaction occurred at a temperature exceeding 550℃ at the third zone. According to our results, the composition of thin films is a titanium metal on stainless steel, polycrystalline $TiSi_2$ on a silicon wafer and amorphous TiSix (x~0.8) on quartz. Among these three samples oxygen is the major contaminant; the atomic concentration of oxygen <5%. In addition, $TiCl_3$ and $TiCl_2$ were obtained as byproducts on the outlet of the reaction chamber. $TiCl_4$ was the volatile residue of the reaction. Furthermore, the total reaction pathway was thoroughly investigated as well.

Keywords: titanium metal thin film, titanium trichloride, titanium dichloride, chemical vapor deposition.

二、緣由與目的

In the formation of integrated circuits (IC's), thin films containing metal are frequently deposited on a substrate's surface. Thin films are deposited to provide conductive and ohmic contacts in the circuits and between the various devices of an IC. A conventional process for depositing thin metal films is chemical vapor deposition (CVD) in which a thin film is deposited using chemical reactions between various deposition or reactant gases at the substrate's surface. In CVD, reactant gases are pumped in proximity to a substrate inside a reaction chamber. The gases subsequently react at the substrate surface, resulting in one or more reaction byproducts which ultimately form a film on the substrate's surface any byproducts remaining after the deposition are removed from the chamber.

Chemical vapor deposition of titanium metal has seldom been mentioned in previous literature owing to the difficulty in depositing the pure metal because it is easily oxidized. $Ti(\eta^5\text{-}C_5H_5)_2$,[1] $Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$, [2]and $(\eta^5\text{-}C_5H_5)TiR_2$ (R=CH_3 and C_6H_5), [3] were used as

the precursors for CVD of titanium. However, even in H_2 plasma, the films were consisted primarily of C. Other examples of Ti deposition are from titanium tetrahalides, TiX_4 (X=Cl, Br, I), by photochemical reaction,[4] high temperature reaction (~1200℃)[5] or using a laser beam[6] to provide energy for the CVD reaction.

In this study, we form titanium based thin films by decomposition of titanium chlorides, were prepared by reacting titanium and titanium tetrachloride at 900℃, at 500~800 ℃. In this reaction titanium initially reacts with titanium tetrachloride to produce $TiCl_n$ (n=1~3) at 900℃. Then, $TiCl_n$ (n=1~3) decomposes to form Ti metal on the substrate's surface at 500~800℃. This study also characterizes thin films, as well as closely examines the reaction pathway.

四、結果與討論

By using titanium tetrachloride as the volatile precursor, titanium metal plate as the reduction reagent, the deposition reactions occurred at a temperature exceeding 550 ℃. Those reactions formed silver gray metallic thin films on the quartz, silicon wafer and stainless steel surface.

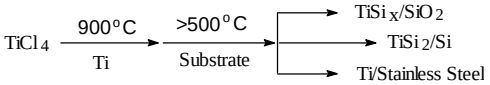
According to our results, the adhesion of thin films on the substrate surface was quite satisfactory (Scotch tape test). Figure 1(a)-(c) illustrate the morphology of thin films grown on silicon wafer, quartz and stainless steel substrates. According to these figures, thin films grown any kind of substrates are planar and uniform. Thin films grown on silicon substrate contains a granular microstructure (Fig. 1(c)). Thin films grown on quartz and stainless steel easily dissolve in dilute acid. Thin films grown on silicon are hard etched by dilute acid. Table 1 lists the reaction conditions, substrates used, thin film compositions and thin film properties.

Energy dispersive spectroscopy analyses show that the major components of thin films are silicon and titanium on the quartz and silicon wafer. On the stainless steel titanium is the major component (table 1). Auger electron spectra analyses confirm the same results. Figure 2 show an auger depth profile of the thin films grown on quartz substrate. For this sample, the oxygen atomic concentration <5% is observed inside thin films.

An X-ray photoelectron spectra survey spectrum of the thin films deposited on quartz and silicon wafer at 600 ℃was obtained before and after sputtering. Figure 3 illustrates the high resolution X-ray photoelectron spectra of the Ti (2p) and Si (2p) region. The binding energies of Ti($2p_{3/2}$) at 454.5 eV and Ti($2p_{1/2}$) at 460.6 eV and Si(2p) at 99.2 eV can be assigned to Ti and Si atoms in an –Si-Ti- network. This observation suggests thin films grown on quartz and silicon substrate are TiSix. On stainless steel, the high resolution X-ray photoelectron spectra of the Ti (2p) reveal the binding energies of Ti($2p_{3/2}$) at 454 eV and Ti($2p_{1/2}$) at 460 eV. This phenomenon indicates that thin films grown on stainless steel are titanium metal.

To elucidate the microstructure of these thin films, x-ray diffraction was employed. The x-ray diffraction pattern indicated that dilute signal in the range 35-45 ° for the thin film grown on quartz substrate. Those results strongly imply that thin films grown on the quartz are amorphous titanium silicide. Thin film grown on stainless steel showed a dilute signal too, it indicated amorphous titanium metal. On the other hand, thin film grown on silicon wafer at 600 ℃ showed sharper peaks that are typical of C54-$TiSi_2$ structure in the JCPDS file.[7] The peaks at 2θ = 23.84, 30.02, 39.18, 42.3, 43.3, 49.79, 67.39, 68.82, 72.02, 76.53, 77.99 and 80.23 belong to the planes (111), (220), (311), (040), (022), (311), (351), (313), (620), (333), (062) and (602), respectively. (Fig. 4)

The reaction results from different substrates can be summarized as follows.



Those reactions form titanium on stainless steel, amorphous TiSix on quartz and polycrystalline C54-$TiSi_2$ on silicon wafer at the

reaction temperature exceeding 550℃. The formation of titanium on stainless steel, indicate the precursor decompose to form elemental titanium. On the other substrates, titanium metal will react with substrate (silicon wafer and quartz) to form silicides at the high temperature (>550 ℃) reaction condition. Herein the amorphous TiSix grown on quartz was easily etched by dilute acid. On the other hand, titanium disilicide grown on silicon wafer are quite stable in the acid environment. The composition of thin films after etch by dilute acid was list in Table 1. Therefore, it is a highly effective means of selectively depositing of titanium disilicide in the fabrication of integrated circuits.

In the outlet of the reaction chamber, purple and brown deposits were found on the chamber wall. The deposits were moisture sensitive, possibly attributed to $TiCl_3$ and $TiCl_2$.[8]

The volatile products, as characterized by mass and infrared spectra, contain titanium tetrachloride ($TiCl_4$) only for the reaction using quartz as the substrate. Extra $SiCl_4$ was obtained when silicon substrate was used as substrate.

In 1993, Kubat employed time-resolved ultraviolet spectroscopy to examine the deposition reaction of titanium from titanium tetrachloride while using an excimer laser.[9] That investigator conjectured that the most probable process for the formation of the titanium film is sequential absorption of photons and the splitting off all the chlorine atoms to form $TiCl_3$, $TiCl_2$ and unstable TiCl, in the final titanium atom.

Other investigators studied the growth rate of titanium film from titanium tetrachloride by excimer laser.[10] According to their results, they proposed two growth regimes. (i) initial growth is attribute to the photolysis of adsorbed $TiCl_4$; and (ii) further growth is owing to thermal decomposition by laser heating. As generally known, TiCln (n = 2, 3) will thermally decompose to form titanium metal and $TiCl_4$ at an extremely low temperature (550~650℃). On the other hand, the deposition reaction of titanium thin films by using titanium tetrachloride as the precursor will occur at 1200 ℃. **Otherwise, the reaction will be initiated by excimer laser.** The phenomenon implies that the most difficult step of decomposition of titanium tetrachloride to form elementary titanium is the initial reduction reaction of $TiCl_4$ to $TiCl_3$.

In this study, titanium metal plate is used to reduce $TiCl_4$ to TiClx (X=3, 2, 1) at 900℃. It is much lower than the thermal decomposition temperature of titanium tetrachloride. Then, further reaction is performed to form titanium at the low temperature area. So, in this reaction the real precursor for titanium will be TiCln (n=1, 2, 3). As general know, $TiCl_2$ and $TiCl_3$ are ionic solids with high melting point, it is hard to introduce them to the deposition chamber. They could not be good precursors for chemical vapor deposition. Excimer laser and high temperature will force titanium tetrachloride decompose to form TiCln (n=1, 2, 3). In this study, we introduce an alternative means to initial the reaction at low temperature and with cheap equipment.[11, 5b]

Conclusions

Introducing $TiCl_4$ into the upstream region with the titanium metal plate leads to the formation of TiClx (X=1, 2, 3), further leading to the formation of elementary titanium film on the substrates exceeding 550℃. This process forms titanium on stainless steel, amorphous TiSix on quartz and polycrystalline C54-$TiSi_2$ on silicon wafer. According to our results, titanium silicide grown on quartz is easily dissolved in dilute acid, allowing for selective deposition of titanium disilicide on silicon wafer at an extremely mild condition (550℃). In this process, no chlorine gas is detected and no hydrogen gas is used; the only volatile component is titanium tetrachloride. This component can be collected and reused. Deposition of titanium from $TiCl_4$ in a thermal process at 1200 ℃ is impossible under conditions compatible with fabricating

integrated circuits. Above results confirm that the proposed method that deposit titanium at 550℃ is highly promising for further device fabrication.

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Table 1 Thin film properties on different substrates at 500℃

Substrate	Etch by dilute acid	Composition (by EDX) Ti	Si	O	ESCA data Ti($2p_{3/2}$)	Si(2p)	microstructure
SiO_2	easy	50	45	5	454.5	99.2	a
Si(100)	hard	27	67	5	454.4	99.1	C54-$TiSi_2$
Stainless steel	easy	98	—	—	454	—	a
C54-$TiSi_2$	hard	66	33	—	454	99	C54-$TiSi_2$
Titanium metal	——	————			454	—	——

a amorphous structure

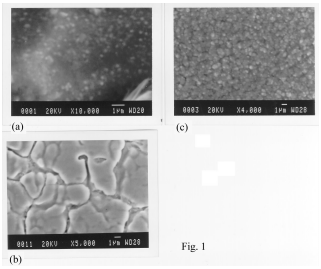

Fig. 1

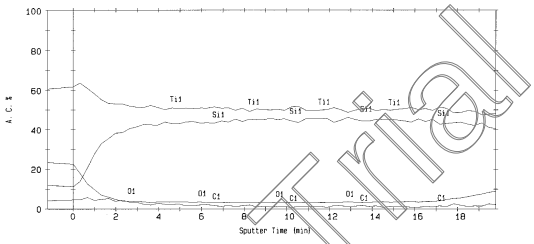

Fig. 2

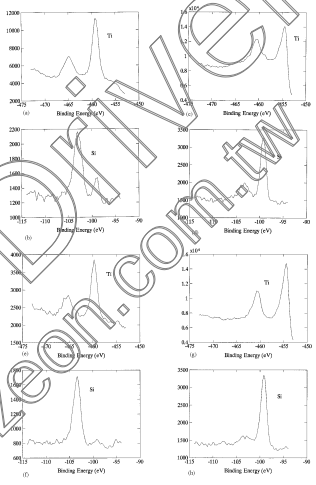
Fig. 3

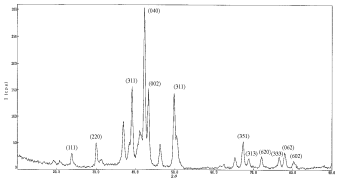
Fig. 4