行政院國家科學委員會專題研究計畫成果報告
二矽化鈦的選擇性成長
Selective deposition of titanium disilicide

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一、中文摘要

二矽化鈦的良導電性以及高溫抗氧化性，使得它成為積體電路中重要的接面材料。其選擇性成長，是以四氯化鈦為前驅物和矽基材反應，在矽基材上做選擇性地成長。但是最大的缺點就是矽基材的消耗量太大，估計每成長的二矽化鈦 1μm 需消耗 7μm 的矽基材。為了改善矽的大量消耗，在成長的過程中再通入適量的矽烷以減少矽的消耗。 結果發現成長的狀況與矽烷和四氯化鈦的流量比，有密切的關係。本研究將以不同的鈦金屬鹵化物(四氯化鈦、四溴化鈦)與矽基材反應，以確實瞭解其反應機制，並尋求最低的矽基材消耗以及最平和的反應條件。

關鍵詞：化學氣相沈積、矽化鈦、四氯化鈦、四溴化鈦

Abstract

The titanium silicide thin films had been formed on Si substrate by reacting of TiX_4 (X=Cl, Br) with Si under different experimental conditions. The Si consumption and the titanium silicide obtains were calculated by the film thickness. In some reactions, titanium silicide thin film was found not only on the Si substrates but also on the SiO_2 wall at the outlet of the reaction chamber. The quantity of Si consumption and the quantity of silicon containing materials obtained on the wall of the deposition chamber varied as the reaction conditions were changed. The minimum Si consumption and the maximum titanium silicide obtains on silicon were the most favorable result. It was found in the reaction of $TiBr_4$ with Si at 1000 . The metalization reactions were studied in detail and the reaction pathway was proposed.

Keywords: chemical vapor deposition, titanium disilicide, titanium tetrachloride, titanium tetrabromide.

二、緣由與目的

The low resistivity of titanium disilicide makes it highly attractive for gate and interconnects metallization.[1] Selective titanium silicide deposition using titanium tetrachloride as a source gas has been reported.[2] Although reacting $TiCl_4$ vapor with Si yields titanium silicide, it is accompanied by excessive Si consumption. This problem has been studied, and silane was introduced into the system to reduce the Si consumption. In those reactions, the titanium silicide film could be controlled to deposited on Si substrates only or on both Si and SiO_2 by adjusting the SiH_4:$TiCl_4$ flow ratios. The large SiH_4:$TiCl_4$ flow ratio causes deposition to occur everywhere not only on the Si. Although the small SiH_4:$TiCl_4$ flow

ratio causes the deposition to occur only on Si, Si had apparently been etched from the surface.[3] $TiCl_4$ is significantly more reactive on Si than that of SiH_4. This low reactivity of SiH_4 accounts for the necessity of large SiH_4:$TiCl_4$ flow ratio for the deposition reaction to reduce the Si consumption.

In this study, we investigate the titanium silicide formation reaction using different metal halides ($TiCl_4$ and $TiBr_4$) as the precursors. The etching reaction of Si with $TiCl_4$ is thoroughly examined under different experimental conditions. Also studied herein is the quantity of titanium silicide formation and the reaction pathway.

三、實驗步驟

The titanium silicide thin films were grown on silicon wafer and SiO_2 substrate in a hot wall LPCVD reactor. Figure 1 schematically depicts the experimental setup. The reactor consisted of a tube furnace, a 30 mm diameter removable quartz tube connected to the precursor inlet system and the pumping system. The substrates were cleaned by the standard procedures to remove grease and the oxide was etched immediately before loading. Substrate temperatures, as measured with a K-type TC gauge, were controlled at 600~1000 . The general procedure for a deposition run initially involved evacuating the system within pressure of 10^{-2} Pa. The reaction chamber was then heated to the desired temperature. After the system evacuated to 10^{-3} Pa, the precursor was vaporized into the reactor at room temperature. The flow rate of TiC_4 is 1sccm and 0.5 sccm. Finally, the volatile products were collected by liquid nitrogen trap and characterized by FTIR and GCMS.

The thin films grown on Si and SiO_2 wall were characterized by SEM for the morphology and by the EDS for the compositions. Several samples were also analyzed by Auger electron spectrometer (AES). The micro-structures of the thin films were characterized by XRD. The quantities of thin films grown on the substrates and the silicon consumption were evaluated by the thickness of thin film and substrates. The gain ratio was defined as the ratio between the quantity of $TiSi_2$ and the consumption of silicon.

SEM was performed in a JEOL 840A microscope, with energy dispersion x-ray analytical capability. X-ray diffraction (XRD) patterns of the thin films were taken with Cu Kα radiation using a Siemens D5000 diffractometer. Infrared spectra were obtained on a Perkin-Elmer PC2000 IR spectrometer. The GCMS data were obtained by a Shimadzu QP1000 spectrometer. Auger Electron Spectrometer (AES) was measured on a Perkin-Elmer PHI-670Xi spectrometer.

四、結果與討論

While reacting $TiCl_4$ and silicon wafer at 600~1000 , the gray and metallic shining thin films were grown on the silicon wafer and reaction wall near the outlet of the reaction tube. According to EDS data, the metallic thin films grown either on the silicon wafer or on the reaction wall contain Ti and Si; the Cl content is negligible as well. The ratio of Ti:Si is about 0.5±0.05. The thin films grown on the silicon wafer and SiO_2 wall both contained polycrystalline C-54 hexagonal $TiSi_2$ phase based on the XRD patterns. Notably, many purple and brown deposits were found on the reaction wall in the outlet of the reaction tube. The deposits

were moisture sensitive, as attributed to $TiCl_3$ and $TiCl_2$.[3] For the reaction temperature range between 600 and 900 , the volatile product is $SiCl_4$. As the reaction temperature rises to 1000 , the volatile products are $SiCl_4$ and Si_2Cl_6.

While reacting $TiBr_4$ and silicon, darkish gray, metallic shining and good adhesive (Scotch tape test) thin films were grown on Si wafer at 800~900 . As the reaction temperature roses to 1000 , the adhesive of the thin films became inadequate. Notably, darkish green and black deposits were observed on the reaction wall in the outlet of the reaction tube. The deposits were deliquescent could be attributed to $TiBr_3 \cdot nH_2O$ and $TiBr_2$. A slight amount of metallic thin films was obtained near the black deposit. The bulk composition and the crystalline property did not significantly differ with respect to the thin films prepared from different metal halides.

Figures 2(a)-2(c) illustrate the morphology of titanium silicide films grown on Si substrate as a function of reaction time using $TiCl_4$ as the precursor. Figure 2(d) illustrate the surface morphologies of titanium silicide thin film grown on SiO_2 wall. Well faceted titanium silicide crystal was obtained on SiO_2 substrate. The film grown on the Si substrate contains a granular microstructure(Fig.2(a)~2(c)). This observation indicates that the grain grew as the thin film grew. This observation also reveals cracks in the titanium silicide film grown on Si with long reaction time. The fracturing occurred in the thick film owing to the difference in the thermal expansion coefficients for titanium silicide and Si substrate.

Figure 3(a)-3(c) display the side view of the thin films grown on the silicon wafer of different reaction time. Apparently, the wave shape was observed in the wafer of a short reaction time (Fig. 3a,3b). For the longer reaction, the surface is flat (Fig. 3c). Those observations reveal crack in the film prepared from high deposition temperature and the long deposition time corresponds to the results from the top view.

Reaction titanium tetrachloride with silicon produced titanium silicide on silicon wafer and quartz wall. Notably, $TiCl_3$ and $TiCl_2$ were observed at the outlet of the reaction tube. $SiCl_4$ was the volatile product detected by FTIR. The formation of $TiCl_3$, $TiCl_2$ and $SiCl_4$ suggests that chlorine migrates from Ti to Si. At a high temperature reaction, FTIR also detected Si_2Cl_6. According to an earlier investigation,[4] Si_2Cl_6 is the insertion product of $SiCl_4$ and $SiCl_2$.

$$SiCl_4 + SiCl_2 \longrightarrow Si_2Cl_6$$

This observation implies that $SiCl_2$ was generated in this reaction. Seebauer(1992) also proposed that silicon absors $TiCl_4$ to yield $SiCl_2$.[5] A later investigation revealed that the most likely compound with a silicon atom in the lower oxidation state is divalent state species, silylene.[6] Obviously, other possible silicon containing species (SiCl and $SiCl_3$)of chlorine migration are also potential candidates.

Herein we propose a plausible reaction pathway to account for how titanium silicide forms on silicon wafer and quartz (Scheme 1). In this pathway, chlorine migration lead to $TiCl_3$, $TiCl_2$, TiCl and Ti, subsequently diffusing to form titanium silicide on the silicon wafer. On the other hand, silicide

forming on quartz accounts for TiCln reacting with SiCln (n=1~4), which might be the chlorine migration products.

Scheme 1

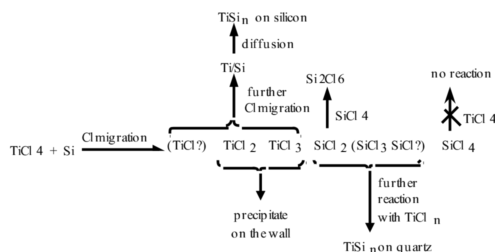

Table 1 lists the reaction condition, silicon consumption, and titanium silicide obtained on silicon and quartz. According to this table the silicon consumption increases with an increasing quantity of titanium silicide grown on quartz. Above observations apparently correspond to the reaction pathway proposed in scheme 1.

Reacting $TiCl_4$ with $SiCl_4$ at 700~1000 with SiO_2 wafer only did not form film on SiO_2 wafer in the deposition chamber. For the volatile collection, $TiCl_4$ and $SiCl_4$ were the only two components detected. The fact that no reaction occurred under these conditions, obviously demonstrates that $SiCl_4$ generated by the chlorine migration reaction did not form titanium silicide on quartz. As assumed herein only silicon containing species (SiCl, $SiCl_2$ and $SiCl_3$) contribute to titanium silicide grown on quartz.

AS generally known silylene is the most likely compound with a silicon atom in the lower oxidation state. The most stable silylene possesses strong electronegative elements. Such substitutes have a strong electron withdrawal form non-bonding electrons of the silicon atom, subsequently producing stabilization.[6] According to this assumption, the life time of dihalosilylene decreases in the series SiF_2>$SiCl_2$>$SiBr_2$>SiI_2. Although the half life of SiF_2 is 150 seconds,[7] that of $SiCl_2$ is microseconds.[8] This observation corresponds to the above assumption. From above discussion we can infer that the half life of $SiBr_2$ is shorter than that of $SiCl_2$.

According to experimental results, the precursor molecules reacted with silicon to form SiXn and TiXn (X=Br, Cl and n=1~3). Those species then passed through the hot zone in the reactor where they further reacted to either form silicide on quartz wall or precipitated on the cold area of the reactor. Experimental results indicated that the quantity of titanium silicide grown on quartz is directly related to the quantity and stability of SiXn. The longer the half life of SiXn implies the more silicide were obtained on quartz. This implication corresponds to experimental observations that reacting $TiCl_4$ with silicon yields more silicide on quartz than when reacting $TiBr_4$ with silicon (Table 1).

五、結論

Metalization of silicon wafer with titanium halides causes titanium silicide to form on the silicon wafer and quartz wall. Results in this study that the lowest metalization temperature is 600 and 800 for $TiCl_4$ and $TiBr_4$, respectively. The yield of titanium silicide on silicon increases with a rise in the reaction temperature. Results presented herein further demonstrate that a higher yield is obtained using $TiBr_4$ as the precursor than using $TiCl_4$. Moreover, the highest yield of titanium silicide on silicon is obtained by reacting $TiBr_4$ with silicon at 1000 . On the other hand, the adhesion of silicon wafer and thin films is inadequate

when prepared at high temperature (1000 for $TiBr_4$ shown in Fig. 3c). The optimal condition appears to be the reaction of $TiBr_4$ with Si at 900 .

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