Summary Abstract: Reactively sputtered RuO_2 and Mo–O diffusion barriers

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Diffusion barriers are indispensable in present very large scale integrated (VLSI) contact technologies to preserve the integrity of shallow junctions and Schottky barriers from Al spiking during postmetallization processing. While a mammoth effort has been devoted to refractory metal nitrides,[1] little attention is paid to the suitability of thin films of conducting transition metal oxides for diffusion barrier applications. This attitude probably springs from the fact that most transition metal oxides are electrically insulating (e.g., TiO_2); some are volatile (e.g., WO_3). There are, however, transition metal oxides that exhibit conductivities at room temperatures. One type of conducting oxide has an oxygen to metal ratio of 2. Two groups can be distinguished. The first one consists of the dioxides of the Pt group metals which crystallize in the rutile structure: RuO_2, OsO_2, IrO_2, and RhO_2. Among the four, RuO_2 is reported to possess the lowest bulk resistivity (about 46 $\mu\Omega$ cm[2]). The other class is made up of the dioxides that adopt distorted variants of the rutile structure: CrO_2, MoO_2,and WO_2. Single crystals of MoO_2 are monoclinic and have a room-temperature resistivity of $\sim 90\,\mu\Omega$ cm.[2] In this report, we summarize the important aspects of the deposition behavior of RuO_2 and Mo–O films formed by radio frequency (rf) reactive sputtering and their diffusion barrier properties against interdiffusion in Al–Si couples.

RuO_2 and MoO_2 are dissimilar in their stability. RuO_2 is the only stable oxide of Ru below 800 °C.[3,7] On the other hand, there exists a higher oxide of Mo which is electrically insulating and volatile (MoO_3).[8] The different oxide chemistry correlates with a different behavior of oxygen incorporation into Ru and Mo films during reactive sputtering. In our sputtering system, RuO_2 films are formed from a Ru target only within a very narrow range of deposition conditions when sputtering in an Ar/O_2 ambient. However, with a Ne/O_2 glow discharge, RuO_2 film deposition can be realized over a wide range of oxygen partial pressures, substrate bias, and sputtering powers.[4] The physics behind sputtering in Ne/O_2 plasmas is elaborated in Ref. 4. The amount of oxygen incorporated into the ruthenium–oxygen alloy films is found to be more or less discontinuous: either Ru or stoichiometric RuO_2 is deposited at one time. The compositions of and the phases contained in the deposited films are confirmed by backscattering and transmission-electron microscopy (TEM) analysis. All the as-deposited RuO_2 films have resistivities near 170 $\mu\Omega$ cm. Contrary to the discontinuous mode of oxygen incorporation into Ru, oxygen can be incorporated into Mo films continuously from 0 to 75 at. % by sputter deposition in Ar/O_2 ambients.[5] Generally, for a fixed initial total sputtering gas pressure, the amount of oxygen contained in the Mo–O films increases with the relative partial pressure of oxygen and decreases with the input sputtering power. All the as-deposited Mo–O films are electrically conducting and polycrystalline, consisting predominantly of Mo and perhaps MoO_2, except for $Mo_{25}O_{75}$ which is composed of a single phase of insulating MoO_3. Such insulating films are formed only under extremely low sputtering power levels or with very high partial pressures of O_2 in the sputtering gas. The resistivity of Mo–O film increases monotonically with their oxygen content (from $\sim 60\,\mu\Omega$ cm for $Mo_{90}O_{10}$ to $\sim 2000\,\mu\Omega$ cm for $Mo_{40}O_{60}$). Mo–O films which are conducting in their as-deposited state remain conducting after annealing (in vacuum or nitrogen) up to at least 900 °C. Sharp drops in the resistivities of all the conducting Mo–O layers are observed for heat treatment above 600 °C. Such annealed layers invariably contain a mixture of the Mo and MoO_2 phases.

Backscattering analysis of a $\langle Si\rangle/RuO_2/Al$ sample shows that Al–Si interdiffusion can be effectively suppressed by the RuO_2 barrier up to 650 °C for 30 min.[6] A $\langle Si\rangle/TiSi_2/RuO_2/Al$ contact structure was tested on n^+–p shallow junction diodes of 0.35 μm junction depth. The diodes exhibit reverse leakage currents that remain unchanged after 30 min heat treatment at 600 °C, but were all shorted after annealing at 650 °C (Fig. 1). This failure is attributed to localized breakdown of RuO_2 barrier undetected by backscattering. Problems of adhesion between Al and RuO_2 can be observed, and result in a slight degradation of the surface morphologies of the contact areas. Mo–O films also act as excellent diffusion barriers between Al and Si.[5] Figure 2 shows the histograms of the reverse current distribution of 40 n^+–p diodes with the $\langle Si\rangle/Mo_{80}O_{20}/Al$ contacts measured before and after annealing at 600 °C for 20 min. (The resistivity of the $Mo_{80}O_{20}$ layer is $\sim 100\,\mu\Omega$ cm.) No junction shorting is observed. Heat treatment is found to affect the surface morphologies little. Although backscattering detects a small outdiffusion tail of Mo in the annealed $\langle Si\rangle/Mo_{80}O_{20}/Al$ sample, this movement of Mo remains very limited up to 40 min anneal-

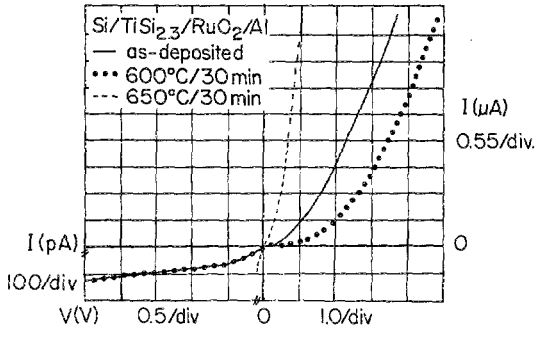

FIG. 1. Electrical characteristics of a typical diode with the $\langle Si\rangle/TiSi_2/RuO_2/Al$ metallization before and after annealing at 600 and 650 °C for 30 min (from Ref. 8).

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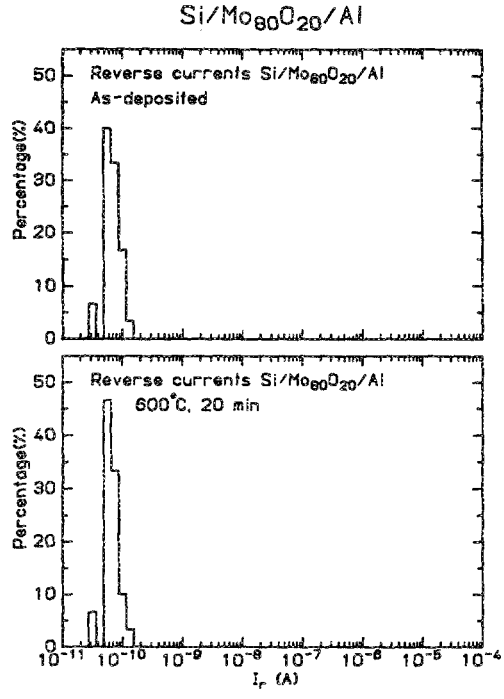

FIG. 2. Histograms of reverse diode leakage currents distributions with $\langle Si\rangle/Mo_{80}O_{20}/Al$ contact before and after annealing at 600 °C for 20 min.

ing at 600 °C. Other Mo–O films containing at least 15 at. % of oxygen are also found to be good barriers against Al–Si diffusion for short time ($\sim$15 min) annealing at 600 °C.

Clearly, both RuO_2 and Mo–O films are effective diffusion barriers between Si and Al even beyond the eutectic temperature of Al–Si (577 °C). Work is underway to investigate the interfacial reactions between the barrier layers and Al.

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