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A Novel Method for Selective Forming SiO_2 on Mo Electrodes and the Film Properties

H. Kyuragi and H. Oikawa

Atsugi Electrical Communication Laboratory, NTT

Atsugi-shi 243-01, Japan

A novel SiO_2 selective formation called the interfacial oxidation method is proposed and proved feasible by experiment. By this technique, a poly-Si/MoO_2/Mo structure can be converted to a poly-Si/SiO_2/Mo by annealing in an H_2 atmosphere and thus, SiO_2 is selectively formed on Mo electrodes. The SiO_2 film formed using this method is shown to have almost the same properties as ordinary thermally grown SiO_2 film.

I. Introduction

Recently, such refractory metals as Mo and W have attracted special attention as materials for gate electrodes and interconnections in VLSI circuits, owing to their low resistivity(1-4). Their resistivity is lower by two orders of magnitude than that of poly-Si. They have, however, two drawbacks compared to poly-Si: (a) their oxidation resistance is low; and (b) insulator film cannot be selectively formed on only their surface. As a countermeasure against the low oxidation resistance, silicidation of Mo surface has been reported(5). In order to solve the insulator film selective formation problem, the authors have proposed a novel SiO_2 selective formation method for use on Mo electrodes, that is called an interfacial oxidation method(6). This method is a technique by which a poly-Si/MoO_2/Mo structure can be converted to a poly-Si/SiO_2/Mo structure through annealing in an H_2 atmosphere.

This paper describes in detail the processing steps in the interfacial oxidation method, and the resulting SiO_2 film properties.

II. Experimental

Substrates were 3 inch silicon wafers with 500 Å thermally grown SiO_2. Mo and poly-Si films were deposited in an electron beam evaporation system. Depth profiles in the sample were measured by Auger Electron Spectroscopy (AES) in combination with Ar ion sputtering. The composition of silicon oxide films formed by the interfacial oxidation method was investigated by X-ray Photoelectron Spectroscopy (XPS). Samples were excited by means of Mg $K\alpha$(1253.6 eV) radiation and 400 W power. Meanwhile, binding energy data were corrected using C(1s) binding energy at 284.60 eV. The thickness of the silicon oxide film formed by this method was estimated from the AES depth profile of the sample and the sputtering rate for thermally grown standard SiO_2.

III. Key processing steps

The key processing steps in this method are shown in Fig. 1. These are as follows:

(a) The Mo electrode is patterned on the substrate and then the MoO_2 layer is formed on the Mo electrode surface.

(b) Poly-Si film is deposited on the MoO_2 layer surface.

(c) A thin SiO_2 layer is then formed sequentially by oxidizing the poly-Si film surface in dry O_2.

(d) Finally, annealing is performed in an H_2 atmosphere.

Note that in this paper the authors refer to silicon oxide formed by the interfacial oxidation method as "SiO_2" to distinguish it from SiO_2 formed by the ordinary thermal oxidation.

IV. Results and Discussion

MoO_2 formation

In the interfacial oxidation method, the molybdenum oxide layer on the Mo electrode surface is used as the supply source for oxidants which oxidize the poly-Si film deposited on the molybdenum oxide layer. There are several kinds of molybdenum oxides, typically MoO_2 and MoO_3. MoO_3 is volatile at high temperature, having a melting point of 795 °C, while MoO_2 is not volatile and its melting point is about 1900 °C.

This method includes a processing step in which annealing in an H_2 atmosphere is carried out at 800 to 1000 °C. Therefore, molybdenum oxide should be stable at high temperature. As a matter of fact, when volatile MoO_3 was used, film pealed off during annealing. Thus, it is necessary to use MoO_2 in this method.

The MoO_2 layer on the Mo electrode was formed as follows. Mo was first oxidized in an O_2 gas at 390 °C to form MoO_3. Subsequently, the MoO_3 was converted into MoO_2 by annealing in an N_2 gas at 700 °C. No weight loss was detectable, within an accuracy of ± 25 μg, either before or after annealing. Therefore, it is considered that MoO_3 hardly sublimates in an N_2 gas at high temperatures and is converted into MoO_2. Consequently, the MoO_3 thickness decides the "SiO_2" thickness.

Role of thin SiO_2 layer on poly-Si film

Figure 2 shows the relationship between the thickness of a SiO_2 layer formed by oxidizing the poly-Si film surface and the thickness of the "SiO_2" layer. If there is no SiO_2 layer, the "SiO_2" became thinner. AES depth profiles after annealing in an H_2 atmosphere showed that MoO_2 was reduced into Mo. It seems that oxygen generated by means of MoO_2 reduction escaped through poly-Si without oxidizing it. On the other hand, if a thin SiO_2 layer was formed on a poly-Si layer surface, the "SiO_2" layer became thicker and could be reproducibly formed. The "SiO_2" thickness scarcely changed over the 70 to 280 Å range of SiO_2 thickness. Since the film pealing was observed locally at the sample surface when the SiO_2 layer became as thin as about 70 Å, the thickness of the SiO_2 layer was fixed to be about 280 Å in this study.

Oxidation characteristics

Figure 3 shows AES depth profiles for the structure both before and after annealing in an H_2 atmosphere for 10-30 minutes at 900 °C. Initial poly-Si and Mo thicknesses were about 1100 Å and 3000 Å, respectively. The MoO_2 thickness was about 700 Å. Before annealing, Auger peak which corresponds to the MoO_2 layer was found at the interface between the poly-Si and Mo layer(Fig. 3(a)). As the annealing proceeded, Auger signal showed two peaks: one on the poly-Si side corresponding to the "SiO_2" layer formed by the interfacial oxidation method, and the other corresponding to the remaining MoO_2 layer(Fig. 3(b)). With further annealing, the MoO_2 layer disappeared, and only the "SiO_2" layer was present(Fig. 3(c)). That is, as the annealing proceeded, MoO_2 was gradually reduced and poly-Si was gradually oxidized from the Mo layer side. Finally, the poly-Si/MoO_2/Mo structure could be converted to a poly-Si/"SiO_2"/Mo structure.

Figure 4 shows oxidation data for the interfacial oxidation method compared to data for the burning oxidation method(H_2:O_2=1:1) and thermal oxidation method with dry O_2. The initial thickness of the poly-Si film was about 1900 Å. The oxidation rate for the interfacial oxidation method was 2-3 times faster than that for the dry O_2 oxidation method, and was almost the same as for the burning oxidation method. It is well known that the difference in oxidation rates between dry and wet oxygen oxidation can be accounted for by the oxidant species(7). Figure 4 can thus be seen to suggest that the oxidant in the interfacial oxidation method is H_2O which is generated by MoO_2 reduction in the reaction:

$$MoO_2 + 2H_2 \longrightarrow Mo + 2H_2O \qquad (1)$$

In wet oxygen oxidation, the oxidation rate changes according to H_2O partial pressure(8). Thus, by changing H_2 partial pressure in this method, one can control H_2O partial pressure and "SiO_2" thickness. Figure 5 shows the "SiO_2" thickness dependence on H_2 partial pressure, while keeping total pressure constant by mixing with Ar gas. It was found that "SiO_2" thickness was proportional to H_2 partial pressure.

Properties of "SiO_2" film

Figure 6 shows the XPS spectra for "SiO_2", compared to that for ordinary thermally grown SiO_2. No other peak associated with Mo was observed over the whole energy range. The Si(2p) binding energy peak agreed precisely at 102.9 eV. Peak width(FWHM) for "SiO_2" and SiO_2 were 2.1 eV and 2.0 eV, respectively. Thus, it was considered that the "SiO_2" composition coincides precisely with that for thermally grown SiO_2.

Leakage current for "SiO_2" film was measured, using Mo-"SiO_2"-poly-Si(-Al) MOS diodes of 500 $\mu m^{\square}$ area. The "SiO_2" film was about 800 Å thick. Leakage current is defined as current with an electric field of 1 MV/cm in the oxide. More than 70 % of the diodes showed a leakage current of less than 10^{-12} A. Breakdown strength, on the other hand, is defined as electric field where there is a current of 1 μA subsequent to application of an 0.5 V voltage step every about 10 seconds. These diodes indicated an average breakdown strength of 3.6×10^6 V/cm. There were also some diodes with values as high as 7.0×10^6 V/cm.

Further, leakage current was measured for "SiO_2" film formed on comb-shaped Mo electrode patterns(Fig. 7). The distance between electrodes, L_2, was 3 μm. Electrode width, L_1, was varied at 5 and 3 μm, in which case the electrode length and number were, respectively, 500 μm and 100. In either case, almost 90 % of the diodes indicated a leakage current of less than 10^{-12} A.

From the above results, it has been concluded that the "SiO_2" film has almost the same properties as thermally grown SiO_2.

V. Summary

It has been found that the interfacial oxidation method enables selective SiO_2 formation on Mo electrodes. A thin SiO_2 layer on the poly-Si surface has increased "SiO_2" thickness reproducibility. The oxidation rate for the present method is faster than that for the ordinary dry O_2 oxidation and is almost the same as for the burning oxidation. Furthermore, the "SiO_2" film has properties similar to those for thermally grown SiO_2 film.

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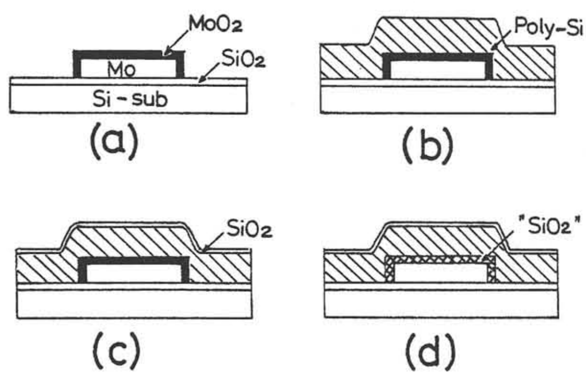

Fig. 1 Key processing steps in the interfacial oxidation method: (a) MoO_2 formation; (b) Poly-Si deposition; (c) Poly-Si surface oxidation; and (d) Annealing in an H_2 atmosphere.

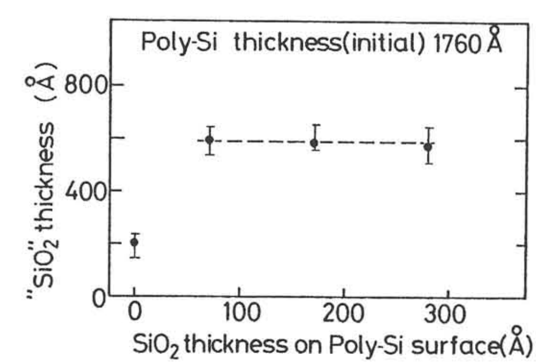

Fig. 2 Relationship between "SiO_2" thickness and SiO_2 thickness on poly-Si surface. Initial poly-Si thickness is about 1760 Å. Annealing was performed in an H_2 atmosphere for 30 minutes at 900 °C.

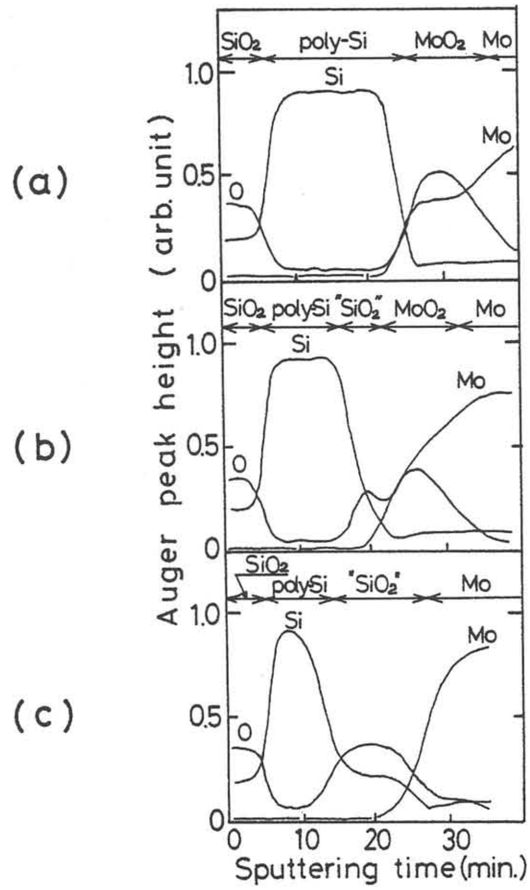

Fig. 3 AES depth profiles for the structure: (a) Before annealing; (b) after annealing in an H_2 atmosphere at 900 °C for 10 minutes; and (c) after annealing for 30 minutes. Initial poly-Si and Mo layer thicknesses are about 1100 Å and 3000 Å, respectively.

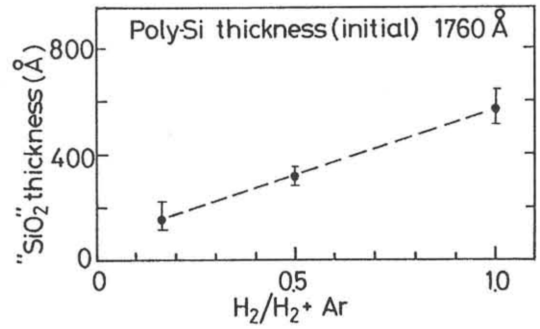

Fig. 5 Dependence of "SiO_2" thickness on H_2 partial pressure. Initial poly-Si thickness is about 1760 Å. Annealing was performed for 30 minutes at 900 °C.

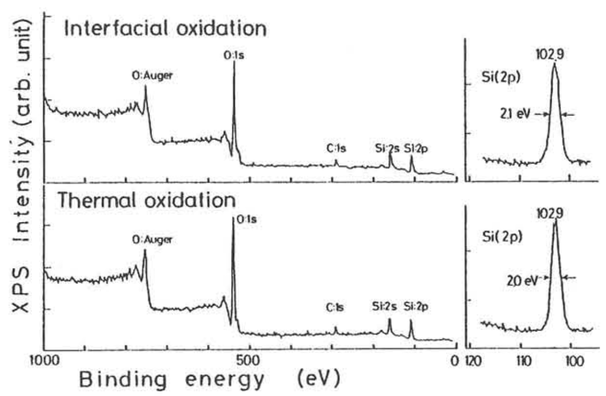

Fig. 6 XPS spectra for "SiO_2" using interfacial oxidation method and SiO_2 implementing thermal oxidation method with dry O_2. Si(2p) spectra are also shown in insert with magnified scale.

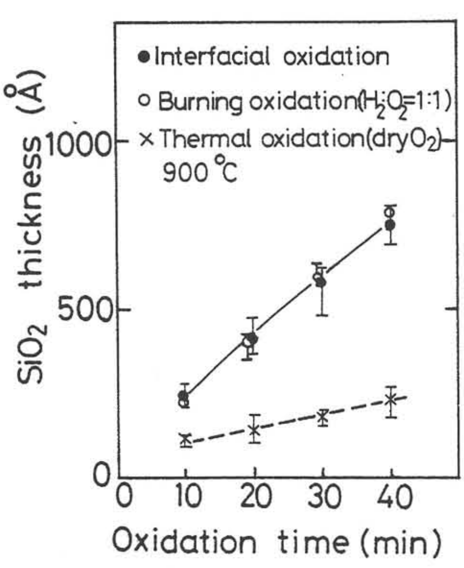

Fig. 4 Oxidation time dependence of SiO_2 thickness. Poly-Si film thickness is about 1900 Å.

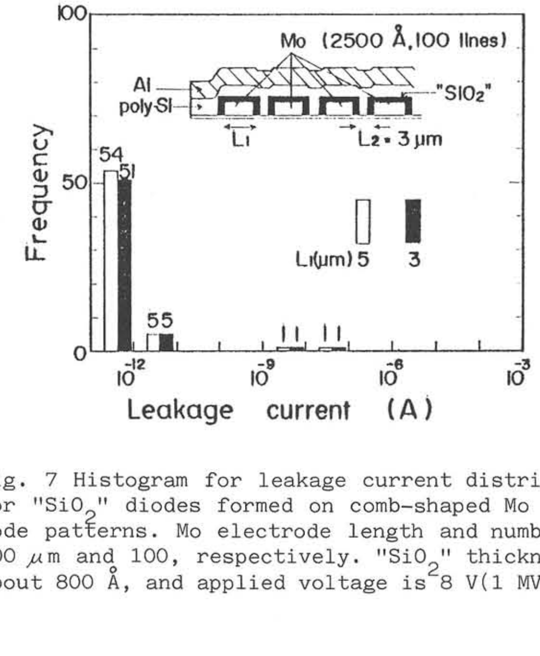

Fig. 7 Histogram for leakage current distribution for "SiO_2" diodes formed on comb-shaped Mo electrode patterns. Mo electrode length and number are 500 μm and 100, respectively. "SiO_2" thickness is about 800 Å, and applied voltage is 8 V(1 MV/cm).