Oxidation of sputtered Cu films during thermal annealing in flowing air

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The article deals with oxidation of Cu films during post-deposition thermal annealing in flowing air. Cu films were sputtered from a pure Cu target in Ar using dc unbalanced magnetron. The copper oxide films formed during post-deposition thermal annealing were compared with CuO_x films sputtered from Cu target in the mixture of Ar and O_2. The oxidation behavior of the films was characterized by high-temperature thermogravimetry and X-ray diffraction (XRD). Thermal annealing was carried out in a wide range of temperatures from 300 to 1300°C. It was found that the CuO oxide decomposes into Cu_2O+O at ~1040° C.

1. Introduction

Recently, it has been shown that a new class of *amorphous Si_3N_4/MeN_x composite films* with high (≥50 vol.%) content of Si_3N_4 phase [1-7] exhibits an excellent oxidation resistance achieving 1500°C; here Me=Ta, Zr, Mo, W, Ti, etc. The oxidation resistance is determined mainly by the decomposition of MeN_x nitride and the crystallization of a-Si_3N_4 phase with the melting point $T_{m\ Si3N4}$=1900°C [8].

However, many applications need the oxidation resistance of the protective coatings to be increased above 1500°C. For such applications protective *amorphous oxide films* seems to be very promising due to their higher thermal stability compared to protective amorphous coatings based on nitrides. A great drawback of ceramic Me^1O_x oxide films is, however, their high brittleness; here Me^1=Zr, Ti, Ta, Al, Si, etc. The brittleness of these oxide films can be strongly reduced by their doping with ductile metals (Me^2) such as Cu, Ag, Au, Ni, etc.

Cu was selected as the doping metal for zirconia (ZrO_2) film in our labs. Unfortunately, only little information is available on the oxidation of Cu at elevated temperatures. Therefore, this article is devoted to detailed investigation of (1) the oxidation of Cu during reactive sputtering process in Ar+O_2 atmosphere and (2) the oxidation of Cu during thermal annealing in flowing air.

2. Experimental

Cu and CuO_x films were deposited using an unbalanced magnetron equipped with target of 100 mm in diameter. More details are given in the reference [8]. The structure of CuO_x films were characterized by X-ray diffraction (XRD). The high temperature oxidation was measured in flowing air (1 l/h) using a symmetrical high-resolution Setaram thermogravimetric system TAG 2400. The mass gain Δm measured after thermal annealing is a measure of the oxidation resistance.

3. Reactive magnetron sputtering of CuO_x oxides

In the case of a deficiency of oxygen atoms, i.e. at low values of p_{O2}, and the number of sputtered Cu atoms N_{Cu} is greater than that of O atoms N_O, the Cu_2O oxide is formed and the sputtered film is the composite of Cu_2O+Cu, see Fig.1. On the contrary, when higher values of p_{O2} (>0.4 Pa) ensuring that N_{Cu}<N_O are used, always the CuO oxide films are formed and even on unheated substrates.

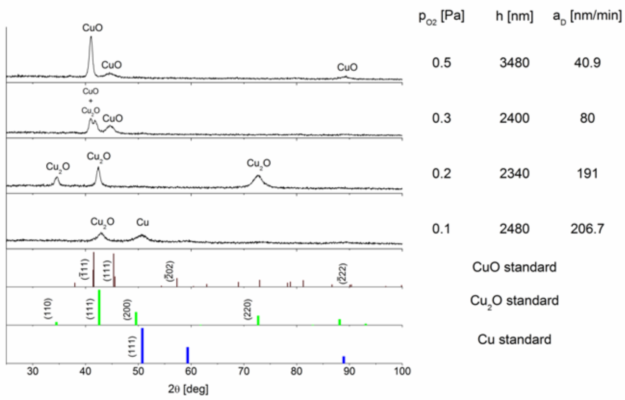

Fig. 1. Evolution of the structure of CuO_x films reactively sputtered from the Cu target at discharge current I_d=1 A, substrate bias U_s=U_{fl}, substrate-to-targe distance d_{s-t}=100 mm, total pressure p_T=p_{Ar}+p_{O2}=1 Pa on unheated glass substrate with increasing p_{O2}.

4. Effect of substrate on oxidation resistance of Cu film

The Cu film is completely converted to CuO oxide during its annealing in flowing air at T_a<1040°C. The CuO oxide is decomposed to Cu_2O+O at T_a=1040°C and free atomic oxygen O can react with the substrate elements. Therefore, the oxidation of the Cu film on the different substrates differs, see Fig.2. The rise of free atomic oxygen O results in a strong oxidation of the Si substrate and due to further formation of SiO_2 from ambient air the mass of the film exhibits a jump increase at $T_a \geq 1040°C$. On the contrary, the free atomic oxygen O does not react with Al because all Al atoms are already bonded in a stable Al_2O_3 oxide.

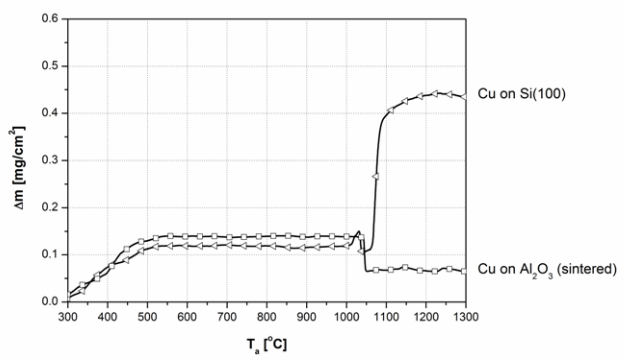

Fig. 2. Comparison of the oxidation of ~500 nm thick Cu film sputtered on the Si(100) and Al_2O_3 substrates.

5. Effect of post-deposition annealing on structure of sputtered Cu film

The structure of sputtered Cu film strongly varies with increasing annealing temperature T_a, see Fig.3. The Cu film is gradually converted to Cu_2O oxide at T_a=350°C and next to CuO oxide at T_a in the interval from 500 to 1300°C. The Cu film thermally annealed at T_a=1300°C is composed of a mixture of two CuO and $CuAl_2O_4$ oxides. The $CuAl_2O_4$ oxide originated from the reaction between the copper oxide film and the Al_2O_3 substrate. The structure of all films was measured after their cooling from T_a down to room temperature (RT).

6. Conclusions

Main results of our investigation of the oxidation of Cu films can be summarized as follows:

1. The pure Cu film can be converted to the CuO film in reactive magnetron sputtering or post-deposition thermal annealing in flowing air if a sufficient amount of oxygen is available, i.e. at $p_{O2} \geq 0.5$ or 10^5 Pa, respectively.
2. The CuO film is decomposed to Cu_2O+O at $T_a \approx 1040°C$. Free atomic oxygen O generated during the decomposition of the CuO oxide can react with elements of the substrate and/or escape from the film. Therefore, the oxidation of the Cu film deposited on different substrates may differ at $T_a \geq 1040°C$.
3. Thermal stability of CuO oxide is determined by its decomposition temperature $T_{decomp} \approx 1040°C$.

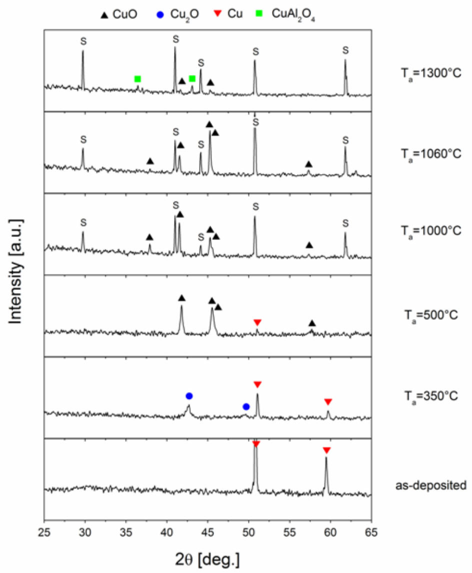

Fig. 3. Evolution of the structure of the ~500 nm thick sputtered Cu film after its post-deposition thermal annealing in flowing air at different values of T_a. The Cu films annealed at $T_a \leq 500°C$ were deposited on the glass substrates and those annealed at T_a>500°C on the Al_2O_3 substrates.

Acknowledgements

This work was supported in part by the Ministry of Education of the Czech Republic under Project No. MSM 4977751302.

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