Sensing properties of W and Mo mixed oxide compounds

E. Comini[1], M. Ferroni[2], V. Guidi[2,3], G. Martinelli[2],
G. Faglia[1], G. Sberveglieri[1]
[1]INFM and Brescia University
via valotti 9, 25133 Brescia, Italy
[2]INFM and Ferrara University
[3]INFN
via Paradiso 12, 44100 Ferrara, Italy

The material properties of the nano-structured materials show remarkable improvement or deviation from the properties exhibited by the coarser grained material. These unique properties are attributed to the significant increase in grain boundary area due to the small grain size. The possibility to manipulate the properties of a nanosized thin film simply through annealing appears to be of widespread interest for material science.

In the gas sensing field of application there is a great effort in reducing the grain dimension and increasing the surface area exposed to the interaction with gaseous species. One of the strategies used is the addition of a second element, which can inhibit the grain growth.
Such a possibility was exploited in the past over WO_3/TiO_2 and MoO_3/TiO_2 thin films. Due to the relatively low sublimation temperature of MoO_3 (~ 800°C) with respect to the melting temperature of WO3 (~1470°C) and TiO_2 (~1800 °C), such systems exhibit a very interesting and complex evolution during thermal treatment. This methodology of preparation of thin films is referred to as selective sublimation processing (SSP). The technical advantages of SSP are manifold. First, grain-coalescence inhibition is expected to take place. As was extensively studied in the past, addition of a foreign element or phase often results in coalescence inhibition of the grains through annealing. Second, the relative proportion of the oxides can be varied when sublimation starts being effective. Third, an effect on film porosity is also expected, depending on the extent of oxide segregation from the nanosized film.

Thin films of Mo and W mixed oxides were achieved by reactive sputtering, assisted by the selective sublimation processing technique. The first results were obtained with depositions from a target of Mo-W with 80%-20% in weight. Deposition of the film resulted in nucleation of Mo oxide in a Mo-W-O amorphous matrix, then the film underwent partial crystallization and oxidation on annealing. A two-phased nanostructure was achieved, featuring sub-stoicheiometric MoO_3 flakes dispersed over a porous W-Mo-O film. Sublimation of MoO_3 was observed, resulting in porosity increase of the layers through annealing. This effect is interesting because it allows one to establish the content of residual Mo ions intercalated in the W-Mo-O film. Moreover, the presence of dispersed Mo and W anions in the WO_3 or MoO_3 phases inhibited grain coalescence upon annealing.
Then a second target of Mo-W with 70%-30% in weight was used and the results of the thin films obtained were compared to the previous one.

Table I reports the characteristics of the layer analyzed. The films were tested as chemo-resistive sensors towards CO at concentration level useful for environmental monitoring and also toward ethanol for breath analyzers and possible interfering gases.

Figures 1, 2 and 3 represent some of the results obtained regarding CO sensing with Mo-W mixed oxide compounds. The responses obtained are remarkable also at concentrations below the alarm level for environmental monitoring.

Table I. Deposition and annealing conditions of the different layers analyzed.

Sensor Code	Target % Mo	Target % W	Annealing [°C]
MoW80/20AD	80	20	-
MoW80/20400			400
MoW80/20500			500
MoW80/20600			600
MoW70/30AD	70	30	-
MoW70/30400			400
MoW70/30500			500
MoW70/30600			600

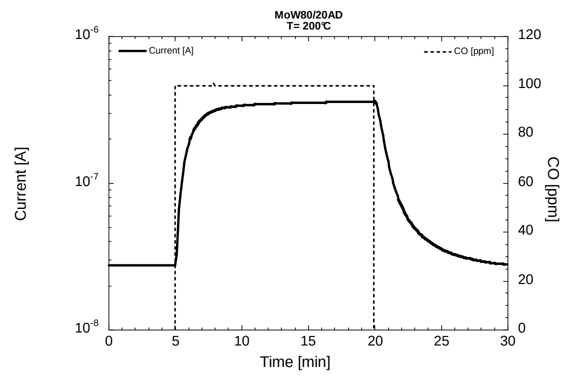

Fig.1 Response of MoW80/20AD to 100 ppm of CO at 200°C.

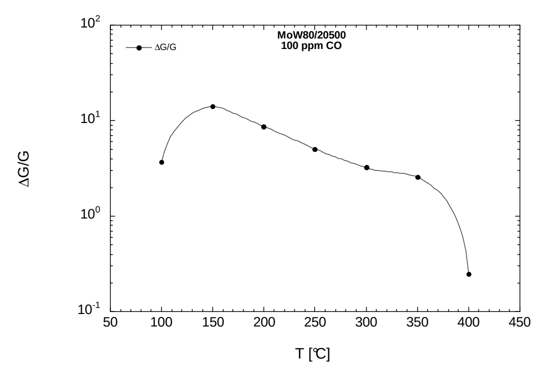

Fig.2 Response of MoW80/20500 to 100 ppm of CO at different working temperatures.

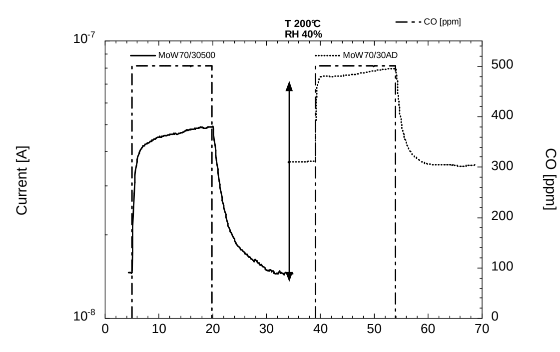

Fig 3 Response of MoW70/30AD and MoW70/30500 to 500 ppm of CO at 200°C