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Interaction of mercury vapour with thin films of gold

C. Battistoni^a, E. Bemporad^b, A. Galdikas^c, S. Kačiulis^{a,c,*}, G. Mattogno^a,
S. Mickevičius^c, V. Olevano^a

^a Istituto di Chimica dei Materiali, CNR, P.O. Box 10, I-00016 Monterotondo Scalo, Italy

^b III University of Rome, Department of Mechanics and Automation, Via C. Segre 60, 00146 Rome, Italy

^c Semiconductor Physics Institute, Goštauto 11, LT-2600 Vilnius, Lithuania

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Abstract

Thin films of gold deposited on a silicon substrate were used as electrical sensors of mercury vapour. The samples were exposed to mercury vapour at room temperature, changing the Hg concentration and the exposure time. The chemical composition and morphology of the films exposed to mercury vapour were studied by X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), scanning Auger microscopy (SAM) and secondary electron microscopy (SEM). In the samples exposed for a short time, the mercury was adsorbed by thin surface sublayer of Au film. In the case of long exposures, the transformation of the uniform Au film to a dendritic-like coalesced AuHg amalgam occurred, i.e. the morphology of the film was modified irreversibly. This transformation is caused by insufficient adhesion of gold to the substrate.

1. Introduction

An increasing awareness of mercury and volatile mercury compounds contamination in the environment has been responsible for intense research of mercury sensitive materials. Gold is well known as a strong absorber of mercury. This feature of gold is widely used for the development of mercury vapour sensitive elements: thin gold film resistors [1], piezoelectric resonators [2], MOS-capacitors [3] and FET's [4]. Gold is also used as a passive collector of mercury, which then can be released by heating and measured by spectroscopic technique [5]. Most of the Au-based mercury vapour sensors exploit the initial phase of the mercury–gold interaction, when few

monolayers of the mercury atoms are adsorbed on the gold surface after the exposition of the sensor to mercury vapour during several minutes. The characteristic time of this process is in the range of 5–30 min and depends on the concentration of mercury vapour. The adsorption of mercury on the clean gold surface can be described by the initial sticking probability, which is close to unity and is decreasing rapidly when the coverage exceeds ~ 0.5 –1 monolayer [6,7]. This model of the initial phase of mercury–gold interaction has been also confirmed by XPS and AES depth profiling experiments [4,5,7]. Nevertheless, according to our knowledge, no attempts have been made to investigate this interaction at long time of Hg exposure, i.e. to check the possibility of the Hg sensing for the long time monitoring of the mercury concentration in air or for the total mercury dose received by men.

* Corresponding author.

This paper reports the results of the study of mercury–gold interaction at the exposures during from few minutes up to one week. The chemical composition and morphology of the samples have been investigated by selected area X-ray photoelectron spectroscopy (SAXPS), scanning Auger microscopy (SAM), secondary ion mass spectrometry (SIMS) and secondary electron microscopy (SEM) techniques.

2. Experimental

Thin gold films were evaporated on the silicon substrates covered with the SiO_2 layer. The film thickness $d = 160$ nm was measured by means of quartz crystal based thickness monitor. The pressure in an evaporation chamber was $P \approx 5 \times 10^{-6}$ mbar and the substrate was kept at room temperature. Then the samples were annealed in vacuum at $T = 300^\circ\text{C}$ and were exposed to mercury vapour in a chamber with controlled air humidity and temperature. The desired mercury vapour concentration in the chamber was obtained by diluting the saturated Hg vapour with air.

The SAXPS depth profiling was performed in a VG Scientific Escalab MkII spectrometer. The analyser's electrostatic lenses were providing photoelectron collection from the sample area of about 3 mm in diameter. The low energy ($E_i = 2.0$ keV) Ar^+ ion beam was rastered over the window (4×4 mm²) in the copper mask. Elemental depth profiles were derived from the areas of the Au $4f_{7/2}$, Hg $4f_{7/2}$ and Zn $2p_{3/2}$ photoelectron peaks. The depth scale was calibrated by sputtering the sample until the substrate and by assuming that the sputtering rate is constant (≈ 0.01 nm/s). More experimental details have been reported elsewhere [8].

The submicron-spot electron gun employed for SAM was operated at 5 keV energy and 10 nA current. Integral Auger spectra $N(E)$ were registered in a constant retard ratio (1:10) analyser mode. Surface chemical images were derived from topographically corrected function $T = (P - B)/(P + B)$, where P is the Auger peak height and B the background height [9].

Dynamic SIMS experiments were carried out by using a VG Isotech MicroSIMS spectrometer with a

magnetic sector analyser. The instrument was operated in low mass resolution mode $M/\Delta M = 300$. The duoplasmatron (O_2^+) source was tuned for low ion energy $E_i = 2.0$ keV. Both optical and electronic gates of the secondary ion optics were activated in order to avoid undesired influence of crater walls.

The SEM images of the samples were acquired by a Cambridge Instruments Leica 360 microscope equipped with energy dispersive X-ray (EDX) analyser, a Link EXL II.

3. Results and discussion

A typical SIMS profile of the gold film exposed for 30 min to Hg vapour with concentration 7×10^{-3} mg/m³ is presented in Fig. 1. The Hg peak is rapidly decreasing and at 5–6 nm is equal to the noise level. Therefore, the mercury is adsorbed only by the thin surface sublayer of Au, which is thicker compared with previously reported results of XPS depth profiling [4,5,7]. The apparently high intensities of the Zn, Cu and C (gold impurities) signals are caused by the SIMS sensitivity, which is very low for both Hg^+ and Hg^- ions (i.e. for the O_2^+ and Cs^+ primary sources) due to the high mass of mercury.

The nonhomogeneous lateral distribution of impurities in the gold film is illustrated by SAM chemical map (Fig. 2). The dark patterns in Hg map correlate with the zones of higher concentration of zinc and/or

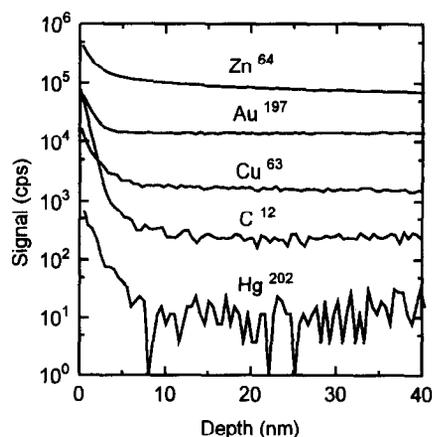


Fig. 1. SIMS depth profile of the Au film exposed to Hg vapour for 30 min.

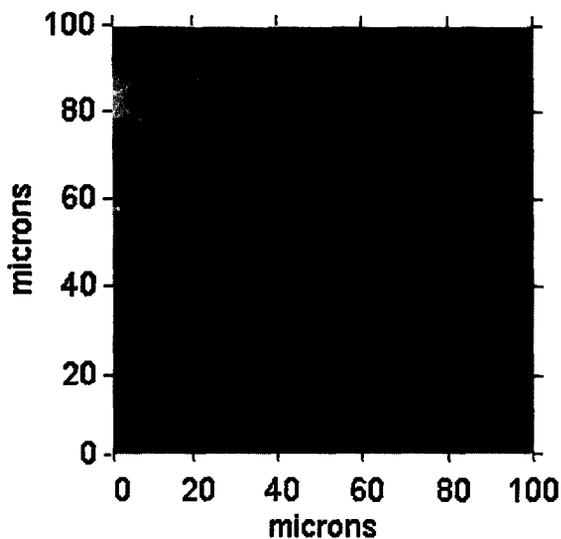


Fig. 2. SAM grey-scale map of Hg on the film surface.

carbon in their chemical maps. It should be noted, that the surface distribution of Hg and impurities (Zn and C) observed in the samples exposed to Hg vapour before and after annealing in air for 30 min at $T = 250^\circ\text{C}$ was quite different. This result is important for the accurate measurements of Hg concentration, if the procedure of mercury collection on gold and desorption by heating is repeated several times.

The SAXPS profiling data of the same sample are shown in Fig. 3. A standard set of the VG ESCALAB elemental sensitivity factors was used in the

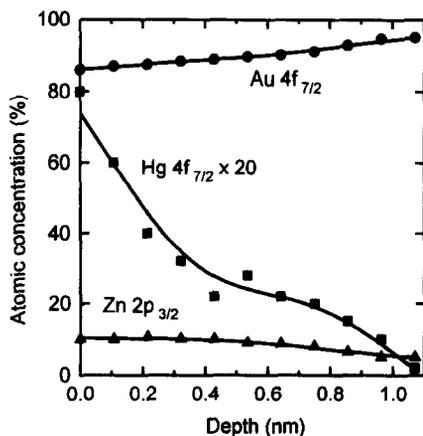


Fig. 3. Quantitative SAXPS depth profile of the Au film exposed to Hg vapour for 30 min. For evidence, the Hg concentration is multiplied by factor of 20.

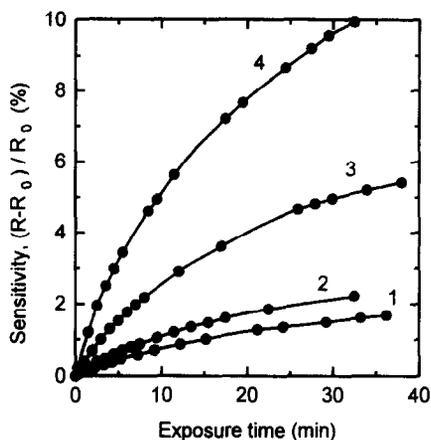


Fig. 4. Time dependence of the Au film sensitivity to Hg at different vapour concentrations: (1) 0.1; (2) 0.2; (3) 0.5; (4) 0.9 mg m^{-3} .

XPS quantification routine including Wagner's energy dependence of photoelectron attenuation length [10]. The rapid decrease of Hg $4f_{7/2}$ peak confirms the SIMS data, i.e. the Hg atoms are really located near to the film surface. Because the elemental sensitivity of XPS is much lower compared with SIMS, the Hg signal is observed only until the depth of about 1 nm. The thickness of the mercury-rich sublayer was independent on the concentration of mercury vapour and did not alter when the samples were kept in air for three months.

The resistance of the gold films slightly depended on the air humidity, i.e. the resistance increased by

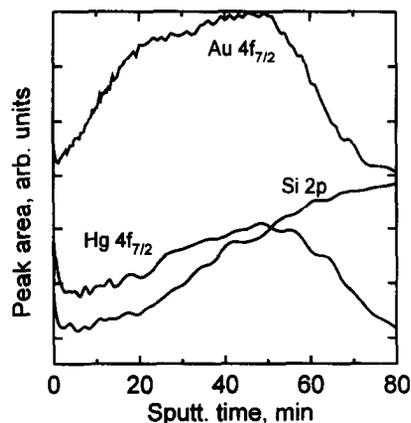


Fig. 5. SAXPS depth profile of the Au film exposed to saturated Hg vapour for 160 h.

~ 1%, when humidity has been changed from 40% to 70%. Therefore, the investigation of the influence of Hg adsorption on the resistance of the films was carried out at constant humidity (60%) and $T = 20^\circ\text{C}$. The dependence of the sensitivity on the time of exposure to Hg vapour is shown in Fig. 4. The time constant of the exponential rise of sensitivity varies from 10 to 30 min.

The SAXPS depth profile of the sample kept in saturated Hg vapour for 160 h is presented in Fig. 5. The mercury and silicon profiles were obtained separating the overlapped Hg 4f and Si 2p (SiO_2) signals by peak fitting illustrated in Fig. 6. Apparent penetration of mercury into the gold volume and the presence of silicon on the surface are caused by the nonhomogeneous disruption of the film. In fact, the SEM image of the same sample (see Fig. 7) exhibits that the uniform gold film was transformed to the three-dimensional dendritic structure of AuHg amalgam. The characteristic width of dendritic branches is about 1–5 μm and the height is about 0.1 μm . These dendrites of AuHg amalgam are weakly

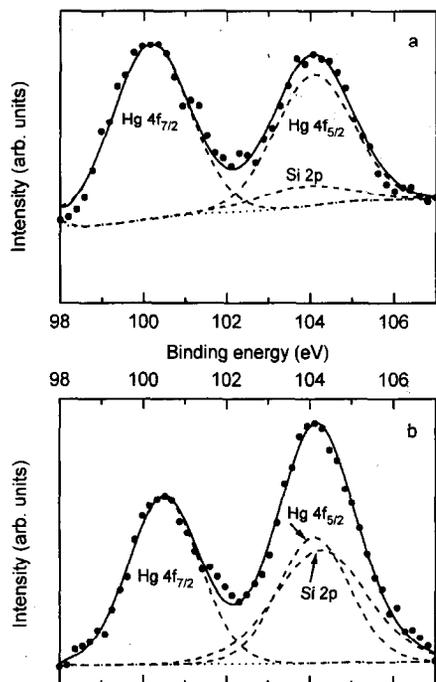


Fig. 6. Evolution of overlapping Hg 4f and Si 2p peaks with sputtering time t : (a) the spectrum at $t = 0$; (b) the spectrum at $t = 50$ min. Dashed curves – least-squares peak fitting.

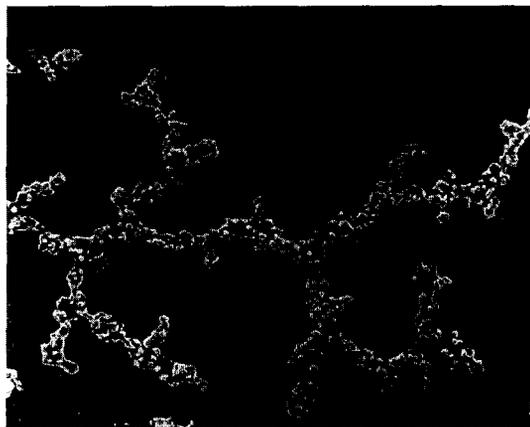


Fig. 7. SEM image of the Au film exposed to saturated Hg vapour for 160 h.

bonded to the substrate and can be easily lost during the sample manipulation (see few darker zones in Fig. 7, corresponding to the uncovered SiO_2). This transformation was also confirmed by EDX and AES multipoint analysis of the sample surface. Both techniques detected the zones of AuHg amalgam and almost uncovered SiO_2 .

The first possible explanation of this unexpected phenomenon is the bad adhesion of deposited polycrystalline Au film to the SiO_2 layer covering the substrate. If the gold is not attached to the SiO_2 , then it can be easily removed and accumulated into dendritic-like structure, when the AuHg amalgam continues to form on the film surface affected by continuous supply of Hg atoms. With this possibility in mind, a simple experiment was performed: a small droplet of mercury has been placed on the untreated sample. SEM photograph of this sample is shown in Fig. 8. EDX analysis confirmed that the very fine droplets in Fig. 8 consist of AuHg amalgam, while the remaining area of the surface is SiO_2 . Consequently, the Au film was disrupted and the whole amount of gold was accumulated in amalgam droplets. The difference of the amalgam structure observed in two samples (Fig. 7 and Fig. 8) is probably related to the speed of amalgam formation. In the sample with a Hg drop on top, the amalgam was formed instantaneously breaking the whole Au film, while in the sample exposed to Hg vapour, the dendritic-like structure of amalgam was formed by

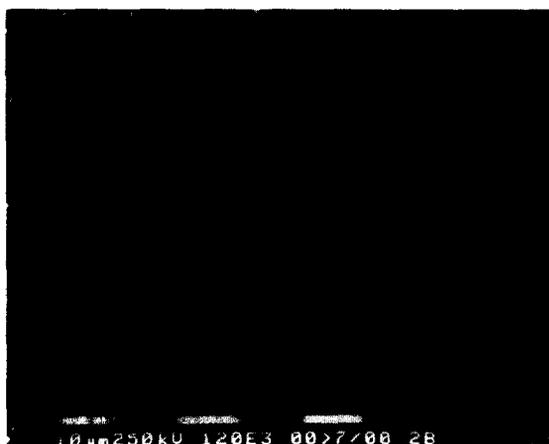


Fig. 8. SEM image of the Au film treated with metallic Hg droplet.

slow process of Hg adsorption. The critical duration of Hg exposure, which is necessary for the disruption of Au film and the ways to improve the film adhesion (i.e. to prevent this disruption) are still under investigation.

4. Conclusions

The multitechnique analysis (XPS, SIMS, SAM and SEM) of Au films exposed to mercury vapour confirmed that the initial formation of only the few monolayers of AuHg amalgam on the surface is saturating the sensor's electrical response. The characteristic time of this saturation is up to 30 min and depends on the concentration of Hg vapour. The sample annealing in air leads to the segregation of impurities on the Au film surface and consequently, to the decrease of Au–Hg interaction, i.e. to the degradation of the sensor's performance. The long

exposures to Hg vapour resulted in the formation of a three-dimensional dendritic structure of AuHg amalgam on the substrate. This phenomenon is caused by insufficient adhesion of gold to the SiO₂ sublayer and must be somehow eliminated, because the irreversible transformation of the film morphology is a serious obstacle in the implementation of Au film-based devices for long time monitoring of Hg concentration.

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