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About the key factors driving the resistivity of AuO_x thin films grown by reactive magnetron sputtering

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Abstract

Deposition of gold containing oxygen thin films was carried out at room temperature onto silicon substrates by reactive magnetron sputtering under Ar/O₂ plasma. Nuclear reaction analysis of films shows that different oxygen concentrations (AuO_x with $x = 0$ to 1.2) can be reached depending on the growth conditions. X-ray diffraction and scanning electron microscopy of the deposited samples evidence nanocrystallised films formed of pure Au phase or of Au metal mixed to a low ordered Au₂O₃ phase. The films display a columnar growth with grains in the 20-30 nm size range. A higher resistivity than that of pure gold is systematically measured by a four probe method. The electrical resistivity of the films was found to be correlated to the mean oxygen amount, and also to the microstructure of the Au phase.

Keywords: gold oxide; reactive magnetron sputtering deposition; thin film growth; electrical conductivity; oxygen content

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Introduction

Several techniques have been investigated to synthesize gold oxide thin films. Nevertheless, only a few studies are available in the literature. In 1970s, Schwarzemann and Fellock described the formation of Au_2O_3 by neutralization of HAuCl_4 solution with Na_2CO_3 [1]. F. Machalett et al. [2] studied the synthesis of gold oxide by reactive magnetron sputtering of a pure gold target under argon/oxygen plasma and found a correlation between the oxygen content in the film and the resistivity. It has been also shown that ion irradiation reduced both, the resistivity and the oxygen content in the film. J.F. Pierson et al. [3] did not show any gas-phase reaction of gold with oxygen during reactive magnetron sputtering in O_2 atmosphere, and concluded on the formation of a pure Au phase from X-ray diffraction (XRD) analysis. In this paper, the oxygen content in the film was not determined. E. Irissou et al. [4] studied the formation of gold oxide by pulsed laser deposition in O_2 atmosphere. XRD analysis evidenced the presence of an Au phase for all conditions of deposition and of an amorphous compound AuO_x (broad peak centered at $2\theta = 32.5^\circ$) when the pressure is higher than 7 Pa. By X-ray Photoelectron Spectroscopy (XPS) they evidenced the presence of Au(III)-oxide at the surface of the film. C.R. Aita et al. [5] detected the presence of AuO^+ and AuO_2^+ ions in the gas phase during reactive sputter deposition of gold in Ar-O_2 discharges. In two other articles [6,7], these authors provided a deep insight in gold oxide film grown by reactive RF diode sputtering, and analysed using XRD and XPS. XPS was essential for evidencing Au-O bond formation : according to the chemical shift observed for the Au XPS peaks, the formation of Au_2O_3 phase mixed with a hydrated form has been suggested, while the XRD patterns only evidenced the (111) planes of the metallic Au lattice [6]. In addition, a large variation of the film resistivity has been measured on films depending on the gas O_2 content in the sputter deposition system, the resistivity being increased by 3 orders of magnitude as compared to the metallic gold resistivity [6].

It seems from the above reported works, that the formation of a well crystallized gold oxide is not possible in conventional deposition conditions of PVD techniques. If no oxide phases can be

unambiguously identified by XRD, detection of a true oxide compound is only allowed by XPS analysis at the outermost surface. If the resistivity of films has already been connected to the oxygen content [2], no correlation with the presence of low ordered oxide phase has been clearly established, to our knowledge.

The aim of the present work is to bring a complementary contribution to the published works on AuO_x thin films synthesized by reactive magnetron sputtering, by correlating the oxygen content in the films with the crystallographic phases and the electrical resistivity.

In the present article, pure gold target is sputtered under Ar/O₂ atmosphere to grow AuO_x films. To study the morphology and the composition of the obtained films, scanning electron microscopy (SEM) and nuclear reaction analysis (NRA) are used. The crystalline properties of the samples are investigated using XRD in θ -2 θ geometry, and the resistivity is systematically measured using the four probe method. Finally, the possible formation of a gold oxide is discussed.

Experimental part

The experimental set-up has been described previously in details [8-10]. The AuO_x films were deposited onto silicon (100) substrates by reactive magnetron sputtering. The target was 4" (101.6 mm) in diameter and was placed 90 mm away from the substrate. The Au metal target was powered by pulsed DC power supply (Pinnacle+, Advanced Energy). The DC power was varied in the range 300–500 W (4-6 W/cm²) to obtain sufficient deposition rates. It can operate in conventional DC sputtering mode or at 150 kHz pulse frequency, with a pulse duration of 1 μ s. O₂ flux was either 3 or 10 sccm and the pressure was fixed between 0.5 and 2.7 Pa. The flux of Argon was varied between 5 and 35 sccm, which leads to a O₂ percentage of flow rate (O₂/Ar+O₂) between 8 and 67 % (Table 1). The total pressure and the percentage of O₂ were varied to tune the concentration of oxygen in the films (AuO_x with x = 0 to 1.2). It can be noticed that in the investigated experimental conditions, a complete oxidation state of gold leading to a pure Au₂O₃ film has not been observed.

The morphology of thin films were examined with field emission gun scanning electron microscopy (FEG-SEM, Zeiss SUPRA 40). SEM observations were performed on both plane and cross-section views to investigate the surface morphology, thickness and structure of the films. NRA was used to study the chemical composition: 900 keV deuterons were extracted from a Van de Graaf accelerator and directed onto the sample to induce the $^{16}\text{O}(d,\alpha_0)^{14}\text{N}$ nuclear reaction. XRD measurements were carried out in a conventional Bragg–Brentano geometry ($\theta/2\theta$) with the Cu $K\alpha$ radiation (Bruker D8). Electrical measurements were performed with the four probe method with a point collinear probe Keithley (6221 DC and AC current).

Results and discussion

1- Composition and nature of phases

The processing parameters used for the growth of thin films are given in Table 1 (pressure, O₂ flow rate %, frequency and power supply, discharge current, and negative bias voltage on the substrate). Several experimental parameters have been scanned in order to incorporate oxygen under different deposition conditions. From typical SEM cross-section micrographs shown in Fig.1, all films exhibit a dense columnar structure constituted with grains in the 20-30 nm size range. The deposition rate determined from the thickness measured on the cross-section SEM micrographs (600 nm), is close to 120 nm/min, whatever the plasma conditions (i.e. whatever the O₂ content in the gas phase and the frequency of power supply), which indicates that no poisoning of the target takes place. [11].

The oxygen concentration in the films, determined by NRA, is reported in Table 1. The concentration of oxygen in the three samples A, B and C is zero. Let us notice that the x value in Table 1 deduced from the NRA measurements corresponds to an average composition over the film, which does not exclude the possible existence of micro-or-nanostructured domains enriched or lowered in one of the element (i.e. metallic clusters in an oxide matrix or oxide phase embedded in a metallic network). The XRD diagrams of these three samples (Fig. 2) confirm the presence of the

single pure metallic Au phase, which has a cubic structure with $a = 0.407$ nm (JCPDS 04-0784) determined from the intense diffraction lines centred at $2\theta = 38^\circ$ and 44.5° ((111) and (200) planes, respectively). At this step, our results are in agreement with J.F. Pierson et al. [3], who concluded to the absence of reactivity of gold with oxygen since no significant modification of the crystalline structure of the metallic thin film was detected by XRD. On the other samples, the NRA analysis gives stoichiometry of $x = 0.25$ (20 at.% in oxygen for sample D), or 1.2 (55 at.% for samples E, F and G). The corresponding XRD patterns (Fig. 2) show the (111) and (200) peaks related to Au phase. In some cases (samples F and G) a broad peak around $2\theta = 33^\circ$ appears, that could be attributed to the (040) or (311) orientations (JCPDS 43-1039) of a poorly crystallized Au_2O_3 phase. This peak could be also attributed to a diffraction peak at $2\theta = 32.57^\circ$ indicated in the JCPDS file (23-0278) of the AuO phase. In their work on gold oxide films grown by pulsed laser deposition, Irissou et al [4] evidenced such a broad peak and, based on their XPS analyses, attributed it to the presence of Au_2O_3 . Even if the presence of an AuO phase cannot be ruled out in the present work, we think that the good agreement we found with Irissou et al [4] results indicates the presence of a low ordered Au_2O_3 phase. The formation of an amorphous gold oxide film by reactive magnetron sputtering has also been related by J.J. Pireaux et al. [12]. In their work, surface analysis techniques such high resolution electron energy loss spectroscopy, Auger electron spectroscopy and XPS were used to show that the major part of gold atoms are oxidized at the surface, OH groups are probably adsorbed at the surface of gold. The presence of an amorphous phase is attributed to the high degree of disorder of the gold atoms which might be agglomerated into small clusters. This behaviour is assumed to be an effect of oxygen diffusion in the lattice. We should note that this study only deal with surface oxidation but no conclusion on the bulk structure of film can be drawn.

The broadening of the peak related to the gold oxide indicates a nano-crystalline or an amorphous state. Indeed, XRD only evidences crystallised phases, meaning that the global composition of film can be influenced by amorphous phases mixed with the Au and Au_2O_3 detected phases. Despite the fact that sample E has the same amount of O atoms as samples F and G, the

(040) and/or (311) XRD peaks of the gold oxide phase are not detected. This could be explained, first, by the formation of a completely amorphous oxide. This has to be correlated to the experimental growth conditions used, especially the bias voltage. An explanation could be the ion bombardment occurring when the substrate is negatively biased. It is known that the energy deposited by an ion flux could induce an amorphisation process of the growing film. A bias threshold value might exist, because at -75 V (sample G), an oxide contribution is still detected in the XRD pattern. Another phenomenon that could explain the absence of the broad peak, despite the high amount of oxygen detected by NRA, is the decomposition of Au_2O_3 with ageing. The instability of this compound has been reported by several authors [2,4,13], and is known to lead to the formation of a nanocrystalline gold phase. It is clearly seen on Table 1 that the full width at half maximum (FWHM) of sample E is larger than that of sample A-C, for which O was not detected. This evidences a lower size of the crystallites and tends to prove that the hypothesis of oxide decomposition after NRA analysis could be valid. It is interesting to note that the FWHM of sample F and G, for which the broad oxide peak is detected, is even larger. This could indicate, in this case, an incomplete decomposition process. It has been shown in the literature that the decomposition kinetic depends on the deposition conditions. Some samples can decompose in three months, whereas others will remain unchanged after several years [2,4]. 8. The decomposition speed also depends on the substrate. A fully oxidized substrate (i.e. quartz or aluminium) cannot more oxidize, whereas for silicon it is possible. So that on silicon AuO_x may decompose much faster due to the oxidation of the substrate with oxygen coming from the AuO_x -film. As a consequence the study of these gold oxide compounds can be questionable, the films being able to evolve between each analysis. However, some trends can be drawn cautiously.

One can notice the Au(111) peak of samples B and C is also broader than that of sample A. Since deposition conditions were different from a sample to another, it is difficult to conclude whether nanostructured Au phase has been formed during deposition or by a post-decomposition of

Au₂O₃. For the gold oxide phase, the high values of the FWHM (more than 5°) confirm a very poor crystallization, the oxide phase can be considered as nearly amorphous.

To conclude this part, it can be deduced that the incorporation of oxygen in gold thin films leads to a broadening of the Au XRD peaks together with the appearance of a low ordered Au₂O₃ phase, for the highest O amounts. The nanostructured Au phase can be formed during deposition but, when oxygen has been used in large percentage in the gas phase (see samples D and E), it is reasonable to think that its formation is rather due to the decomposition, during ageing period, of a previously formed Au₂O₃ phase.

2- Electrical properties

The two parameters that could play a role on the resistivity are the Au phase grain size and the presence of a poorly conductive phase, such as an oxide. Since the electron mobility is mainly ensured by metallic conduction along the Au grains, the presence of a high density of grain boundaries will lower the conductivity and thus leads to higher values of the resistivity. In the case of biphasic film, the total conductivity depends upon the electron mobility through the various pathways available in the materials, which defines a percolating network. Percolation theory indicates that an electrical property is effective for a percolation threshold above 25% [14]. It means that the resistivity of the Au metallic matrix should dramatically increase in a few orders of magnitude if the concentration of the isolating Au₂O₃ phase reaches 25% at least. This corresponds to globally 40% of oxygen atoms present in the gold film.

On Fig. 3a, a clear correlation is observed between the resistivity and the FWHM of the gold phase. A broadening of the XRD peaks reveals the presence of small size crystallites that means, of extended grain boundaries. Thus, the evolution on Fig. 3a evidences the negative influence of the grain boundary density on the electron conduction. It is known that voids, defects and even amorphous oxide phases, may exist between the Au grains that impede the mobility of electrons. In Fig. 3b the evolution of the resistivity with respect to the oxygen percentage in the film is displayed.

Two different trends are observed: for low oxygen contents (below 40%) the resistivity of films is close to that of pure gold, and above 40% very high values are found, which, however, stay below the value reported for Au₂O₃ (see Table 1). This study shows that the resistivity is related to the oxygen amount in the film. However, this sole parameter is not sufficient to conclude on the existence of an oxide phase in the films. It appears clearly from our results that a strong correlation exists between the electrical properties and the crystalline quality of the gold phase.

We can deduce from our investigations that Au₂O₃ phase is formed in reactive magnetron sputtering of a gold target when O₂ is present in the gas phase above 50%. Because of the instability of this phase towards ageing, the measurement of the O content in the film may not reveal that the as-deposited film has been firstly oxidized. Nevertheless, since this oxide decomposition leads to the formation of a nano-crystallized Au phase, a kind of fingerprint of the previously existing Au₂O₃ phase still exists. We think that some of our troubling results (see samples B and E, for instance) are due to the evolution of the films between each analysis. Thus, a high resistivity does not mean that an oxide phase is present, but may be an indication that it has been previously formed. Moreover, taking into account both parameters - oxygen content and Au phase crystallinity - may be useful to predict the electrical conductivity evolution of gold films, since the presence of Au₂O₃ or its destruction leads to an increase of the resistivity.

Conclusion

In this study, we have investigated the reactive magnetron sputtering deposition of gold in Ar/O₂ atmosphere. Deposited films are composed of a nanostructured Au phase and, in some cases, of a low ordered oxide phase attributed to Au₂O₃. The resistivity was measured in order to correlate electrical conductivity with physical features of the films. Some of the obtained results appear questionable at first glance, like the absence of oxide phase when oxygen is present in high amount in the gas phase or is detected inside the film. This is tentatively explained by the tendency of Au₂O₃ to degrade with time. Our observations are in agreement with available literature and show

that this decomposition leads to the formation of a finely divided Au phase. In such films, the grain boundary density is so high that it yields to an increase of the resistivity.

Finally, a high value of resistivity of gold films cannot be only correlated to the amount of O in the film and the presence of an oxide phase. The existence of a fine nanocrystallized Au phase will have the same effect on the electrical property, thus both parameters have to be taken into account to understand the film behaviour.

Acknowledgement

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Table caption

Table 1: experimental parameters of deposition; composition and electrical resistivity of the samples; FWHM of the Au (111) diffraction peak

Table 1

| Sample | % O2 | Power (W) | Frequency (kHz) | Target current (A) | BIAS substrate (V) | Pressure (Pa) | Composition | Resistivity ($\mu\Omega\cdot\text{cm}$) | FWHM Au(111) (Deg.) |
|--------------------------------|------|-----------|-----------------|--------------------|--------------------|---------------|---------------------|---|---------------------|
| A | 23 | 300 | 0 | 0.60 | 0 | 0.5 | Au | 4 | 0.13 |
| B | 50 | 300 | 150 | 0.60 | 75 | 0.5 | Au | 21 | 0.64 |
| C | 8 | 500 | 0 | 1.07 | 0 | 2.7 | Au | 10 | 0.55 |
| D | 50 | 500 | 150 | 1.07 | 75 | 2.7 | AuO _{0.25} | 43 | 0.84 |
| E | 50 | 300 | 150 | 0.70 | 150 | 2.7 | AuO _{1.2} | 1120 | 1.16 |
| F | 50 | 300 | 150 | 0.70 | 0 | 2.7 | AuO _{1.2} | 2180 | 2.28 |
| G | 67 | 300 | 150 | 0.70 | 75 | 2.7 | AuO _{1.2} | 6330 | 2.45 |
| | | | | | | | | | |
| Bulk Au | | | | | | | Au | 2.44 [2] | |
| Au ₂ O ₃ | | | | | | | AuO _{1.5} | 5000000 [2] | |

Figure captions

Figure 1: Typical SEM micrographs (cross-section on left, top-view on right) of thin films deposited on Si substrate

Figure 2: θ - 2θ XRD patterns of films with composition ranging from Au to AuO_{1.2}.

Figure 3: Plot of the resistivity vs (a) FWHM of the XRD Au(111) peak, (b) O ratio in the films as measured by NRA (note the vertical log scale)

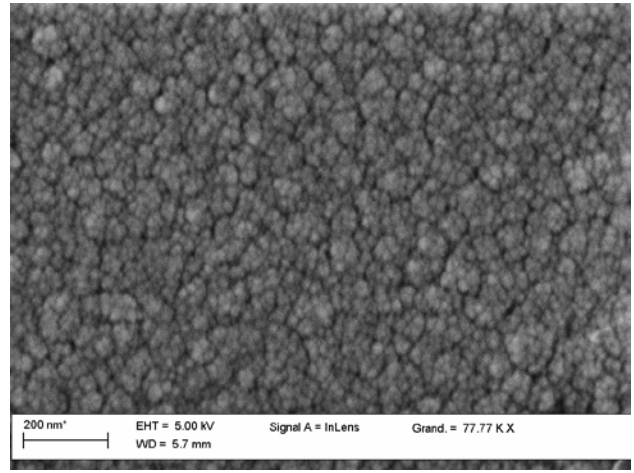
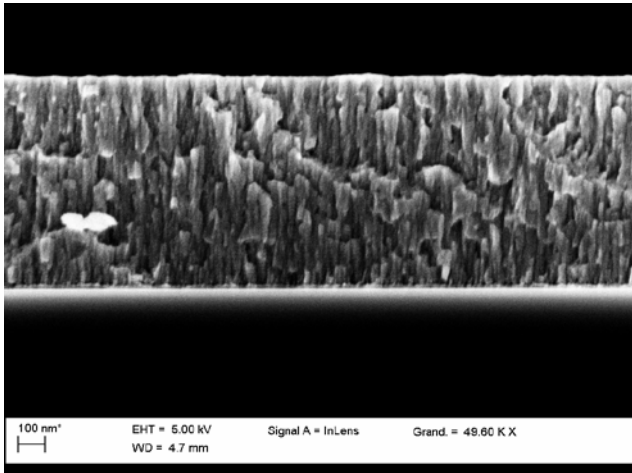


Fig. 1

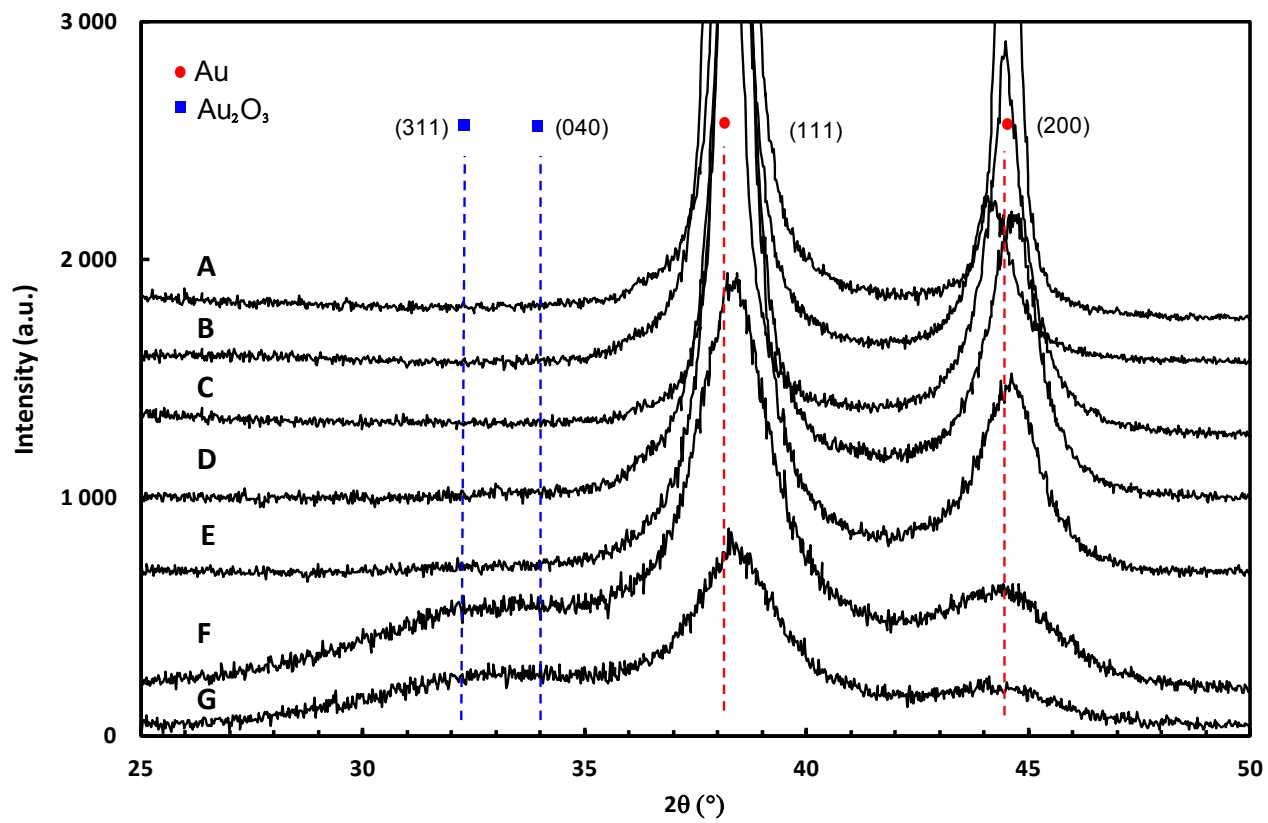


Fig 2

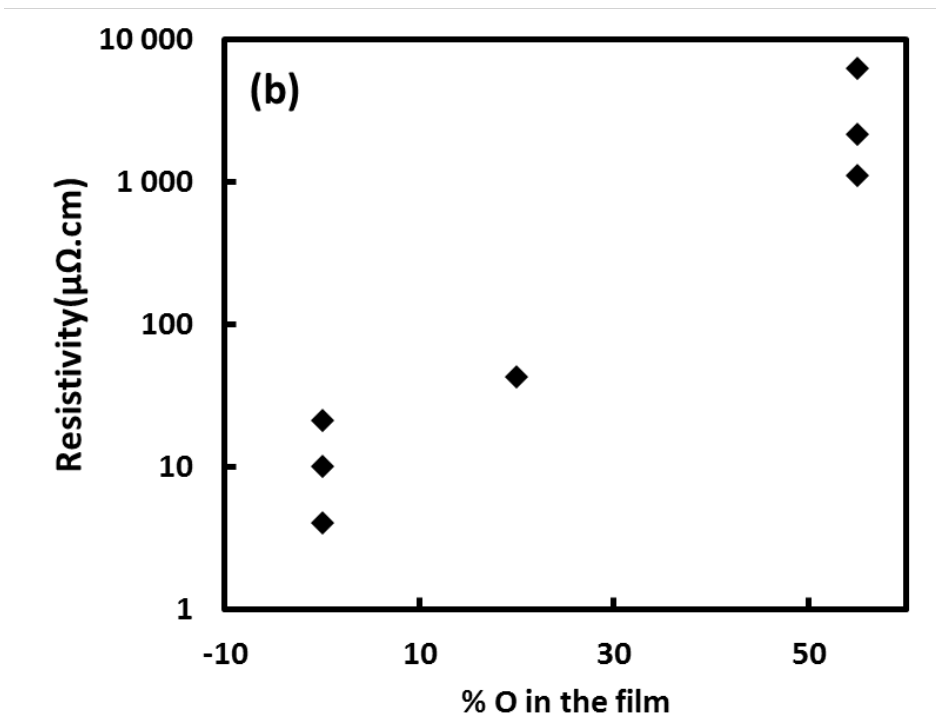
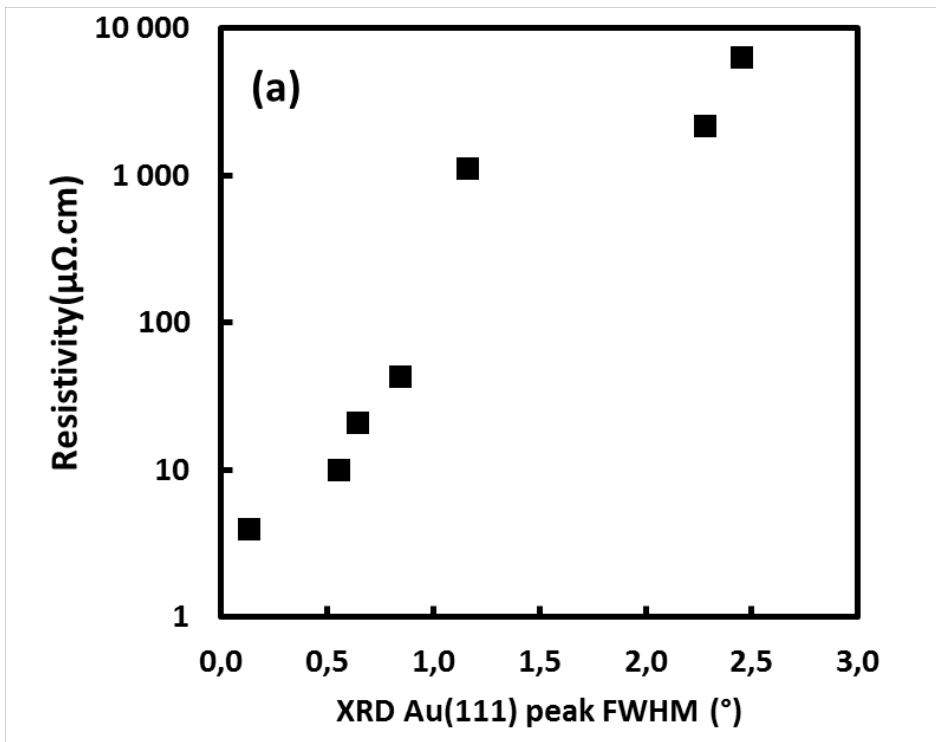


Fig. 3