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Thin Metal Films in Resistivity-based Chemical Sensing

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Abstract: Thin metal layers are widely utilized in a number of modern applications in electronics, optics, chemistry and many other applications. At present the thin layers of metals serve in applications spanning from simple electrodes to surface plasmon resonance (SPR) or giant magnetoresistance (GMR) based sensors [1, 2]. Thin films allow monitoring redox processes in the vicinity of electrodes, adsorption/desorption equilibria of ions, organic compounds, gases, and more recently also interactions of large organic macromolecules such as proteins or DNA. In a previous review we have covered applications of thin films in biosensing regardless of the measured physical change [3]. Measurement of basic electric properties (current, voltage, resistance) is simple and precise with large dynamic range. Since the related equipment is simple and inexpensive; such sensors might be very attractive for many applications in chemistry, environmental sciences or medicine. In this work, we shall discuss the potential of metal layers for future applications in resistance based chemical sensing.

Keywords: Chemiresistor, thin metal film, voltohmmetric sensing, gas sensing.

INTRODUCTION

Preparation of Thin Metal Layers

Deposition of metal layers on other materials is one of the most often used technology processes. Gold ornaments have been crafted on artworks for thousands of years. Later on in the industrial age a plethora of technologies have evolved into an important field of surface modifications.

Evaporation – first reported by Edison in bulbs with carbon filament, later Faraday [4, 5] (1857) described wire exploding when heated by high electric current. More recently Holland and Mooser reviewed the technology in detail [6-8]. Vacuum evaporation method is still widely used due to its simplicity and reproducibility. In this method, the metal target is heated in a chamber where the pressure is maintained between 10^{-4} and 10^{-6}Torr. At this pressure the mean free path of the gas atoms in the chamber is between 0.45 to 45m.This corresponds to physical dimensions of the vacuum chamber. As the heated metal evaporates the vapors condense on the colder surface of the coated specimen. Depending on the construction and application a number of evaporation modes can be distinguished.

In *Resistive heating* the material to be deposited is in contact with filament made of W, Mo, Ta or Nb with or without ceramic coating. For indirect heating material is situated in a boat or in a cruciblemade from quartz, alumina, zirconium, beryllium or thorium ceramics.

Flash evaporation – is another method especially developed for multicomponent evaporation, where fractional distillation of the alloy needs to be suppressed. It is realized by dropping fine powder of target material continuously on heated boat and quick vaporization of the powder continuously supplied by a vibrating mechanism. This method is very sensitive to input conditions and suffers from poor reproducibility.

Arc evaporation – is a suitable method for evaporating refractory metals such as Ni, Ta, W and more. This method was widely used for carbon evaporation for use in electron microscopy, but deposition of metals is difficult to control.

Exploding wire– not widely used method for electric evaporation of metals. It leads to evaporation and quick plasma forming in the working region. The coated surface may be hit by some of the coarse particles of the target metal or nonvaporized drops of melted metal.

Laser evaporation – this promising method is well suitable for evaporation of many materials, especially high temperature melting metals, oxides, ceramics and more. Virtually any material can be evaporated by this method. Target material is in bulk or powder form, focused laser is localized in region of few μm, so it is also suitable for automated and precisely controlled multicomponent sputtering. There is minimal risk of contamination; layers made by this method are of the high purity and quality.

Electron bombardment heating –is similar to laser evaporation in results. High intensity electrons are focused on target material to ensure its evaporation. In some modifications, this method is used also for electron beam welding and marking.

RF heating – the material is heated by electrical induction at a kHz rate. Inductive coil can be made in a special arrangement, where the target material is levitating inside the coil, to ensure high purity of the evaporated layer by preventing contact between target material and RF coil. This method is not widely used in laboratory practice, but well established in industrial metallurgic processes.

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In *Sputtering* – atoms are extracted from target material by strike of energetic particles accelerated against the target. When the energetic particle is positively charged, this method is called cathodic sputtering as opposed to anodic sputtering with negatively charged particles. This phenomenon was first reported by W. R. Growe in 1852 [9] and Plücker in 1858 [10]. Over the years, the main disadvantage of this method (contaminations coming from impure gas in the chamber at relatively high pressure)has been overcame, and currently it is the most widely used method in laboratory and industrial practice as well. In present apparatuses the discharge chamber is filled with neutral gas, *e.g.*, Ar at pressures in the range of 10^{-3} - 10^{-1} mbar. Many nonmetallic materials can be also sputtered.

Principles of a Conductivity Thin Film Metal Sensor

In a regular metal conductor such as a round wire with the diameter of several micrometers or more the direct electric current (DC) flows uniformly across the wire cross section. The electric resistance of such a wire depends mainly on its length, diameter, material and temperature. The surface changes related to chemical interactions have little influence on the wire resistance unless its diameter is reduced, *e.g*. by corrosion. In case of an alternating current of sufficiently high frequency (MHz and more) the current starts to be transported mainly at the surface of the wire. This so called skin effect [11] is important in high frequency electronics. The thickness of this “skin” layer depends on frequency and may be potentially useful also for future sensors. As the diameter of the wire or the thickness of a metal layer decreases to the dimension comparable to the mean free electron path (MFP) the DC electric resistance starts reflecting also the interactions on the metal surface.

PHYSICAL PROPERTIES OF THIN METAL FILM, CONDUCTION MECHANISMS

Continuous Metal Film

The main parameter in characterizing the electrical conductivity in metals is the *mean free electron path* (λ) described as:

$$\lambda = v\tau = \frac{\hbar k}{m}\tau \tag{1}$$

Where v is the velocity and τ is the collision time, $\hbar k$ is the de Broglie’s momentum of a quantum wave and m is mass of the electron. The mean free electron path is a characteristic constant depending on the material and temperature, *e.g.*, 39 nm for copper at room temperature [12,13]. In general, the minimum thickness of the metal layers should be more than 5 nm. Below this limit the film is practically discontinuous with islands like structure - see Fig. (**1**). With decreasing thickness, resistivity of the metal layer increases, when the thickness becomes comparable to the MFP. This is also one of limiting factors in building ultra large – scale integration electronic devices [14]. The transition between thin and bulk behaving is not well defined – see Fig. (**2**). With increasing thickness of the layer, it behaves increasingly more like bulk material determined by changes in conductivity, not caused by processes occurring at the surfaces- Fig. (**3**) [15]. Similarly to the light propagation in an optical fiber two main events play a role in electric conduction in thin films - the specular reflection and diffuse electron scattering [16].

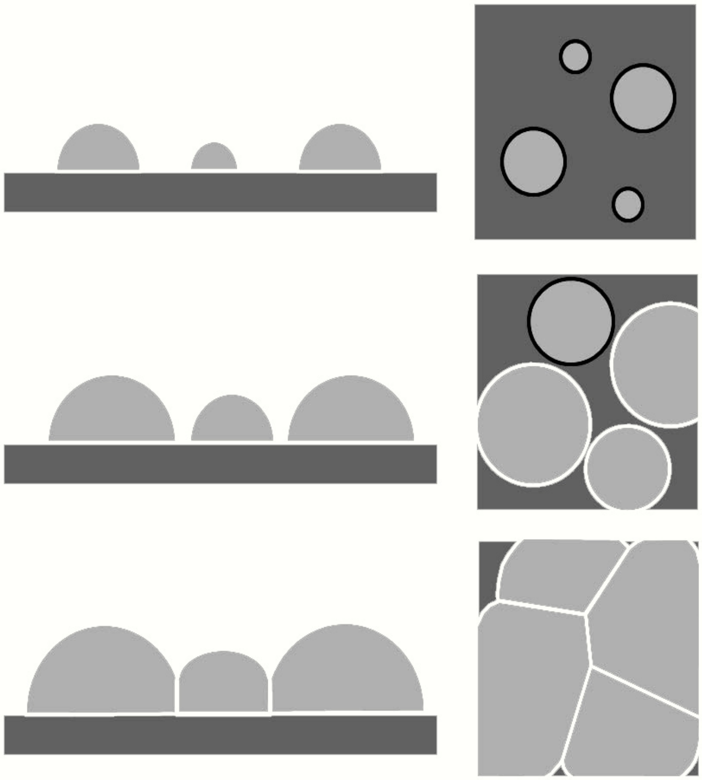

Fig. (1). Island structure of deposited metal film; Nucleation, growth and coalescence to form a continuous film. Schematic diagram displaying (**a**) cross-sectional and (**b**) plain-sectional sketches; Redrawn from reference [17].

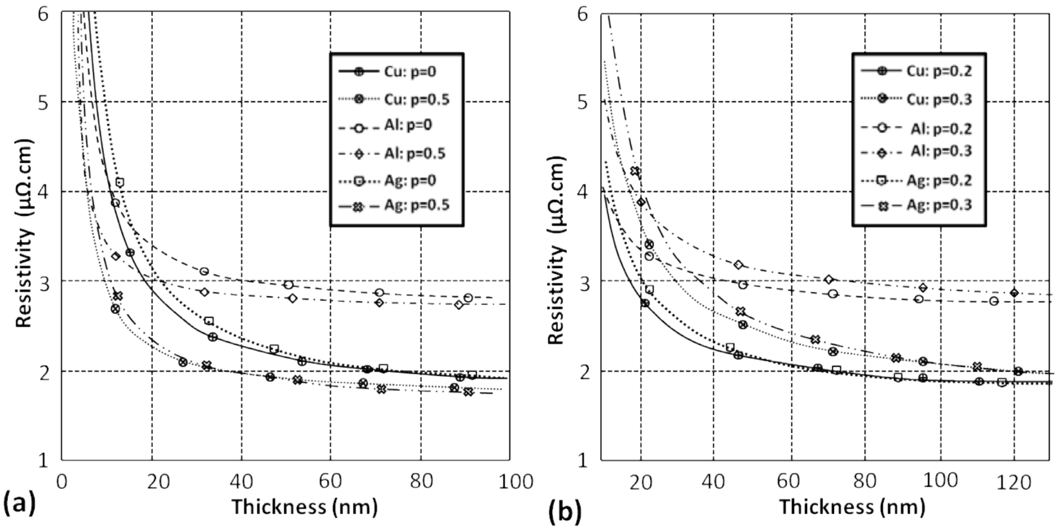

Fig. (2). Calculated resistivity of Ag, Cu and Al thin layers based on Fuchs – Sondheimer model (a) and Mayadas–Shatzke model. Simulation show the resistivity increases slowest with decreasing film thickness. Redrawn from reference [14].

Diffusely scattered electrons are reflected stochastically without preserving their velocity and momentum and do not participate on electric current flow anymore. The diffuse scattering plays the main role in the bulk resistance of the metal film. In *Specular reflection* electrons are reflected at the physical boundary of the metal layer with angle of reflection equal to the angle of incidence. Their velocity and momentum is preserved. The overall resistance of the metal film is influenced by a number of factors including: 1) defects of the crystal lattice, such as dislocations, vacancies, impurities, grain boundaries, etc. 2) phonon associated with surface waves, 3) termination of the charge carrier wave function at the surface 4) charge gradient due to presence of the surface states5) The physical appearance of the surface layer – surface defects and physical nonidealities, mainly roughness of the film, 6) variation of angle of incidence of the carriers to the surface and changing number of scattering events and 7) chemical characteristics of the surface layer. Detailed treatment of the individual factors involved in the charge transport is described elsewhere [17-19]. Here we'll focus on some important properties related to interactions on the thin layer surface.

Specularity parameter*"p"* is an empirical constant [16, 21-24] expressing the probability of the specular scattering. The supplement of *p*, *(1-p)* is the probability of the diffuse scattering, *p*=1 for ideal specular scattering and *p*=0 for ideal diffuse scattering. According to Ziman's model, the value of *p* rapidly decreases when film thickness *d* decreases to a value comparable with *λ* (MFP). Very rapid decrease of the *p* parameter was also observed, when surface roughness exceeds 45 Å [22].

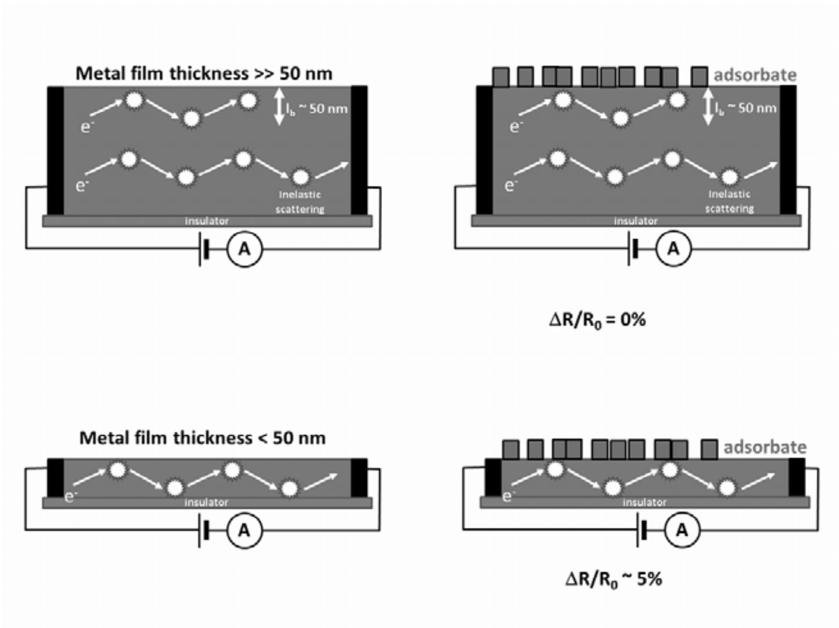

Fig. (3). Change in resistance as a function of the thickness in resistive sensors. When the thickness is high (upper figure), the electrical resistance does not change because the inelastic scattering events in the bulk predominate. When the thickness of the metal film is low (lower figure), the adsorbed target molecules can be detected by measuring the change in the electrical resistance. Redrawn from reference [20].

Temperature coefficient of resistivity (TCR)

The resistance of metals changes with temperature. The characteristic coefficient of the temperature change α is described by eq. (**2**), where ρ_0 corresponds to the specific resistance temperature coefficient at a specified reference value (normally T = 0 °C).

$$\alpha = -\frac{1}{\rho_0}\frac{\partial\rho}{\partial \mathrm{T}} \qquad (2)$$

The temperature coefficient of resistivity (TCR) α_ρ and the temperature coefficient of resistance α_R are equal, when thermal expansion coefficient α_T is negligible, because $\alpha_\rho=\alpha_R+\alpha_T$. This condition is true for bulk metals, but for thin films the thermal coefficient correction became significant. This phenomenon is well described and is frequently used for temperature measurement as a thermistor or microbolometer [25]. Due to the considerable value of TCR, chemical sensors working on a principle of resistivity change have to be thermally compensated, thermostated or mathematically corrected to a reference temperature. Often a combination of mentioned methods is used.

Properties of freshly prepared film – The electrical conductivity of the metal film may be strongly affected by absorption and adsorbtion of gases and other impurities during the film preparation. Beeck *et al*. [26] noted, that vapor deposited Ni films, prepared in vacuum had significantly lower resistance compared to sputtered films prepared in presence of Ar or N_2. Similar result was observed by other authors for more metals and for other gases present in sputtering chamber. This phenomenon is caused by occluded gas atoms in the metal layer and by porosity at the atomic scale. These assumptions were confirmed by mass spectrometry analysis and ion bombardment of the film samples [19]. In practice, this side effect is surpassed by holding the substrate at elevated temperature during sputtering or by thermal post treatment. There is another phenomenon that contributes to the high initial resistance of sputtered layers - a large number of structural defects in the freshly prepared layer, *e.g*. (dislocations, vacancies, stacking faults *etc*.). Additional factor is the existence of grain boundaries. If the grain sizes are similar or smaller than the MFP they significantly contribute to electron scattering and result higher electrical resistance of the layer. In general, thermal treatment of the layer gives a noticeable and irreversible decrease of electrical resistance, which is caused by gas desorption, sintering and growth of the grains. Resistance drop during annealing of Au film was reported to be 50% of its original value during heating at 400°C for 60s period by passing electric current [27].

Monocrystalline film – Films with near to ideal properties are prepared by epitaxial growth during vacuum evaporation onto monocrystalline substrates. Freshly cleaved mica sheets and Si wafers are mostly used for this purpose. In general, atomically flat substrate is needed for this method, so Si wafers have to be super polished. The substrate is held at elevated or ambient temperature during evaporation. Evaporation is performed at low rate, typ. less than 1nm/min and after evaporation wafers are annealed at 400K or higher for 1h or more. Due to less absorption and adsorbtion of impurities, the annealing conditions do not need to be as drastic as in the case of the sputtered films resulting in atomically smooth or terrace-like look of the layer with well oriented planes. Metal layers were prepared with orientation (111) on mica [28] and Si; (100) on Si; (001), (101) and (110) on more exotic substrates including Au on Fe – (110), Mo on NaCl – (110), Au on GaAs – (011) and (001) [17, 29-31].

Characterization of Thin Films

Depending on the application there are many methods for characterizing of the thin metal layers including *optical methods*- elipsometry, interference, transmittance and reflectance methods. Special case of the optical measurement is the surface plasmon resonance (SPR), which can be used for very precious measurements of adsorbtion of molecules on the free surface of the layer including lab-on-chip analysis [32]. *X-ray microscopy* – is used for detailed and non-destructive chemical analysis of the film in the scale from 0.25 µm down to 10 nm [33].

Electron diffraction methods –are used for characterizing the crystal structure of the layers [34,30]. *Scanning electron microscopy* – (SEM) is one of the most common methods for quality control of the surface and chemical composition more recently complemented by *Atomic force microscopy* (AFM) –[35, 36] and *Scanning tunneling microscopy* (STM) [37-39].

Adsorption on Metal Films

Three basic processes are mainly responsible for resistance changes of the thin metal layers: a) adsorption affects the number of free electrons in the metal layer [40], b) adsorbed substances generate new scattering centers of the surface layer [41], c) adsorbed substances react with the metal and de facto reduce the effective thickness of metal film by a single atomic layer [42, 43]. For mechanism a) it is assumed, that surface adsorbtion only affects the number of free electrons in the metal film expressed by eq. (**3**)

$$-\frac{\Delta G}{G} = x'\left(\frac{N_a}{N_e}\right) \qquad (3)$$

Where $\Delta G/G$ is the relative change in conductivity, N_e is total number of free electrons in the metal, N_a is number of adsorbed molecules at surface, x' is proportionality constant. Value of the constant x' depends on fraction of electrons accepted by the metal and correlates with electron affinity of the adsorbate to the metal. When the electron affinity of the adsorbate is higher with respect to the metal, then adsorption causes decrease of the film conductivity and vice versa.

For the mechanism b), it is assumed, that the change of the surface resistivity ρ_f is directly proportional to the adsorbate surface concentration T_{ads} as expressed by eq. (**4**) [18].

$$\Delta\rho_f = K_0\Gamma_{ads} \qquad (4)$$

Last adsorption mechanism under consideration is based on scenario c), where the film thickness d is variable, but specularity parameter p, mean free path λ, and the number of free electrons in metal film is constant. By reactions occurring at the surface the thickness of the film is lowered by the value *Δd*. This dependence is expressed in the eq. (**5**), where ρ_b is resistivity of the bulk metal.

$$\Delta\rho_f = -\left(\rho_f - \rho_b\right)\frac{\Delta d}{d} \qquad (5)$$

Field effect–When an external electric field is applied to the layer, it affects the conductance of the layer by changing its surface charge density. Since the electric field of the adsorbed molecules is in order of atomic dimensions, the effect becomes noticeable only when thickness of the layer is in the order of the MFP. For gold layers it was found that the conductivity changes linearly with the applied field [44-46]. In an interesting experiment it was observed, that the charge induced by metal cations at the outer Helmholtz plane increases the resistance. This was confirmed by another experiment, where the water layer adjacent to the gold film was replaced with amyl alcohol weakening the interactions and increasing the separation distance of the charged layer. During desorption of the alcohol, the resistance changed back up to the value corresponding to the base electrolyte. Similar results were obtained also for other organic compounds [47].

Design of the Resistivity Sensors

The simplest circuit for chemiresistive sensing is a two terminal probe – Fig. (**4**). As mentioned in the previous text, this arrangement has its main disadvantage in strong temperature dependence of the resistance, which has to be preciously thermostated, calibrated or both. In the most simple two terminal arrangement in Fig. (**4a**) the constant current source is connected across the thin film metal element and the resulting potential drop is monitored by a voltmeter. In an ideal case, as long as the temperature and current are kept constant, the monitored voltage will change upon the analyte binding on the metal surface.

Temperature dependence of the signal can be suppressed by using the *Wheatstone bridge* Fig. (**5**), where one of resistors –R_{Ch} is substituted by the chemiresistor. Under ideal conditions, this device is temperature compensated. When constructed with discrete resistors having different temperature coefficient of resistivity (TCR) than that of the chemiresistor, residual temperature dependence will still be present. This can be practically eliminated by preparing the whole bridge element in one step from the same thin metal film.

Additional designs have been developed for more complex measurements, such as the five terminal probe, allowingsimultaneous measurements, such as 2-point and 4-point sensing [48]. In these devices, usually counter electrode, reference electrode and working electrode are implemented to the system.

Additional combined arrangements have been described in the literature including the one with a Hall sensor termi-

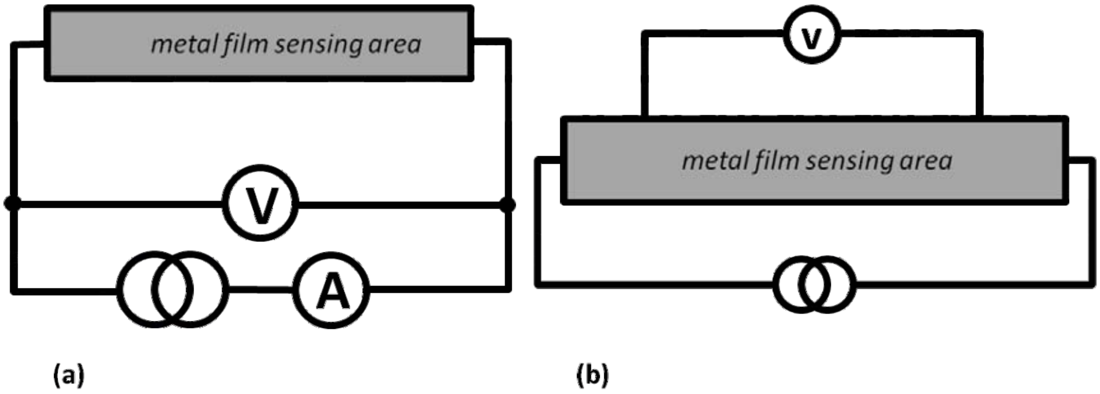

Fig. (4). Two terminal chemiresistive sensor A more robust four terminal arrangement in Fig. (**4b**), where the voltage change can be measured just from the sensing section eliminating the parasitic resistances of non-sensing parts of the circuit.

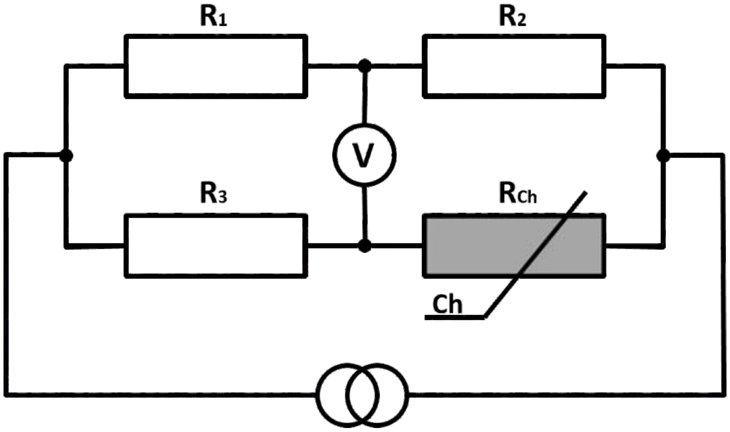

Fig. (5). Chemiresistive sensor in the Wheatstone bridge circuit.

nals in the centre of the chip for studying behaviour of electrical double layers at electrode surfaces [49].

Beside the measurements based on the DC current, the AC mode can be also used. In some cases the AC measurement can provide increased sensitivity, better stability and noise discrimination; however the AC measurements are sensitive to changes in double-layer impedance in highly conductive solutions [50].

Gaseous Adsorption on Metal Films

While adsorption of an analyte on the thin metal film sensor can be monitored in any fluid state the gas phase sensors are much more developed and tested for analytes ranging from mercury vapours to large organic molecules. Chemiresistive sensors for measurement of Hg vapours based on the thin gold layer were reported first in 1978 [27]. When mercury adsorbs onto the gold film, its conductivity decreases. As the coverage of the sensor surface increases, the signal starts to deviate from its initial linear response to saturation. With 10nm gold layer the reported sensitivity was on the order of 10 μg m^{-3} mercury vapour. This sensor can be regenerated by heating to 150°C. Unfortunately, cross-sensitivity to atmospheric moisture and sulphuric compounds reduces its selectivity. Sensitivity to water vapour was determined as 1% change in resistivity, corresponding to change in relative air humidity from 40 to 70% [51]. This problem was reduced by covering the gold film with a monomolecular alkanethiol layer acting as a molecular filter [52]. Current commercial sensors working in the integration mode exhibit dynamic range of 1 – 1 000 pg/m^{-3} for for Hg vapours and 3 – 500 ppb for H_2S, with the response time of 13s. These sensors are practically insensitive to moisture, SO_2 and hydrocarbons [53].

A different family of chemiresistors are sensors for detection of *volatile organic compounds* (VOC), which were first reported in 1968 [54]. These sensors, although belonging to the chemiresistor family, are working on a slightly different principle. The typical construction comprises two electrodes in an interdigital design overlaid by a thin film of semiconductive organic polymer or a composite material [55] Fig. (**6**). In one arrangement, the change of conductivity is caused by charge transfer from reaction between the vapour and semiconducting film, which affects number of carriers in the conduction band. This sensor is limited to detect only species, which are suitable electron acceptor or donor. A different sensor is based on micrometer or nanometer-size conductive particles dispersed in the polymer matrix. Microparticles used in this system are typically carbon black or vanadium oxide in a matrix such as (polyethylene, polystyrene, poly(vinyl alcohol) or poly(vinyl chloride)) [56]. In the most recent applications carbon nanoparticles, carbon nanotubes, metal nanoparticles (NPs) (spheres, nanowires) are being investigated. In an example depicted in Fig. (**6**) the dispersed particles were gold spheric NPs with sizes in the range of few nm to ~100nm. The Au core had an organic shell, typically containing thiolated functional group end bonded to the NPs. Chemiresistive effect of this type of sensor lies in swelling of the matrix containing conductive NPs, which effectively lengthens the particle to particle distance in matrix and decreases its conductivity based on electron tunnelling or hopping between nanoparticles [57, 58]. Conductivity of this Au NPs nanocomposite is strongly affected by the length of the organic chain in the shell molecule. This provides a mean for conductivity optimization in a wide range [59, 60].

Although these sensors achieve sensitivity in the ppm range they still suffer from relatively low selectivity and sensitivity to air humidity. The selectivity issue can be effectively solved by using array of sensors with various shell substances, giving typical fingerprint of the analytes. Such a system was successfully tested for use as a gas chromatography detector [62]. The humidity problem can be minimized by using strongly hydrophobic chains in the shell material and by calibration [63]. For precise measurement the AC technique is preferred, minimizing the residual drift of the resistance, which is believed to be caused by slow electromigration of nanoclusters to the electrode surface [60].

An interesting approach was recently described by D. H. Read and J. E. Martin. The chemiresistive sensor for VOCs detection was built from gold-plated nickel nanoparticles in PDMS matrix – Fig. (**7**). During curing of the resin, the PDMS substrate was placed into a uniform magnetic field of 650 G. That oriented particles into chains parallel to the substrate. By application of the tensile strain the resistance of this sensor can be reversibly changed and the reported sensitivity has improved 55-fold with respect to the original value. This technique can be also used in combination with an actuator for dynamic tuning of the sensor and wider dynamic range [64]. More recently, AuNP based chemiresistors

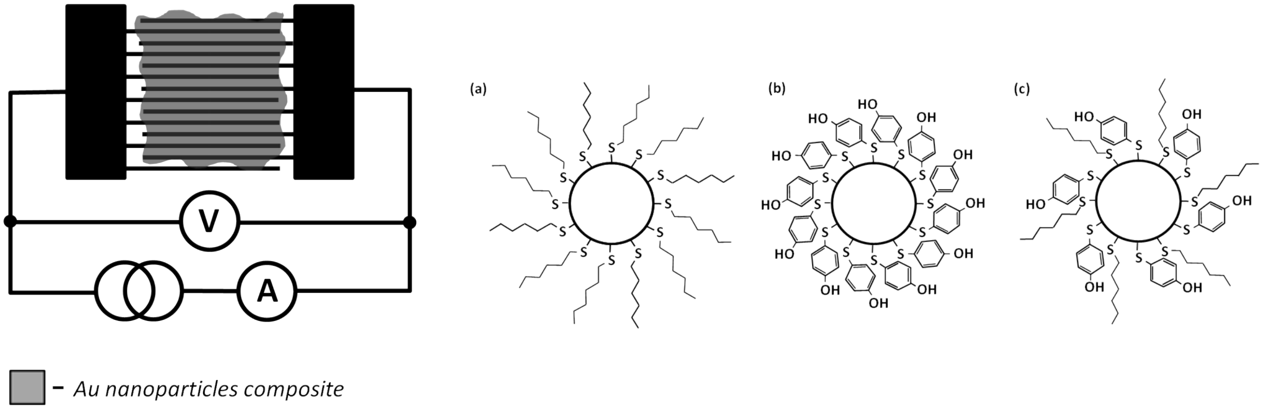

Fig. (6). Scheme of the VOCs chemoresistive sensor based on Gold nanoparticles. Gold nanoparticles were modified with (**a**) 1-hexanethiol, (**b**) 4-mercaptophenol and (**c**) a mixture of 1-hexanethiol and 4-mercaptophenol. Redrawn from reference [61].

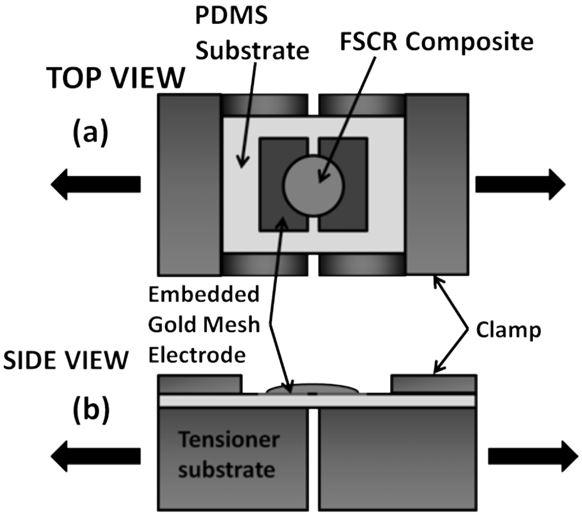

Fig. (7). Schematic view of the VOCs chemiresistive sensor with tuned sensitivity Redrawn from reference [64].

were successfully used for lung cancer diagnostics by detection 4 of 42 VOC's in breath as a biomarker, which are present in healthy patient at level 1-20ppb or at elevated level of 10-100ppb in cancer patient [65, 66]. Similar application of AuNPs chemiresistors was described for fingerprint detection of VOCs in water [67, 70] or organic contaminants in fuels [71].

Thin Film Metal Layers for Sensing in Liquids

While the gas phase sensing is quite an advanced technology, chemiresistors for sensing in liquid phase are in an early stage of development. In fact, the main interest in the past years has been focused more on the semiconductor nanovires, carbon nanotubes and nanoparticles rather than on the metal films [72]. In the past Niki and Shirato [73] studied conductivity changes of the gold film electrode as a function of potential. Electrodes were in contact with n-amyl alcohol or benzoic acid solutions. Maximum resistivity change occurred at the potential of zero charge (PZC). It was also found, that with respect to base electrolyte for n-amyl alcohol the conductance decreases and for benzoic acid rises. In another work [74], adsorption of thiourea, urea and hydrogen sulphide on Pt electrode in the presence of H_2SO_4 were conducted. Addiction of thiourea during the potential sweep between 0.05 and 0.8V led to sudden increase of resistance and further slow increase during cyclic polarization. Resistance of Pt electrodes which were covered by thiourea was practically independent on the potential in the range of 0.05 - 1.0V. The authors concluded that the small value of potential dependence after adsorption is due to bond strengtening with time and increase of resistance during adsorption is mainly caused by adsorbed sulphur atoms after splitting of the C-S bond. This was experimentally verified by measurement of adsorption of H_2S on Pt films. It was found, that for thiourea and hydrogen sulphide the resistance change is similar, but is small for urea. Tucceri and Posadas [75] studied adsorption of pentan-1-ol on gold electrodes. They made complete thermodynamic analysis based on the Gibbs adsorbtion isotherm, obtained coverage by organic compound at constant electrode charge and behaviour of this alcohol was quite similar to diethyl ether on the polycrystalline gold electrode. It was supposed, that this alcohol adsorbs on the gold surface identically as at the Hg surface, where are molecules arranged with hydrophobic ends facing to the Hg surface. However, free energy of adsorption at gold is much lower for pentanol resulting in weaker chemical interactions in comparison to Hg surface. The main effect of the alcohol results from isolating the metal from the electrolyte and change of the surface charge.

Ionic adsorption on metal films - There are many papers investigating the ionic adsorption. In general, electrical conductivity decreases with increasing degree of adsorption. It was suggested by Mansurov [76]**,** that for weak adsorption the resistance change is determined by the change of the free surface charge, but for strong adsorbates it is mainly caused by fixation and scattering of the conduction electrons and change of the effective thickness.

Adsorption of halogenides - When the potential of metal electrode is increased in the positive direction, the resistance change is rising to its limiting value, which follows the same series as the adsorbability on the gold electrode ($F^- < HSO_4^- < Cl^- < Br^- < I^-$). It was concluded, that each ion has its own limiting value of surface coverage $T_{ads.lim}$. For the Br- ion an exception was found, where the resulting value of ΔR/R depends on the concentration of Br- in the electrolyte, see Fig. (**8**). In this case the value of $T_{ads.lim}$ was attributed to be dependent on the Br- concentration [77]. It was also found, that the ΔR/R change for Cl- is two times larger than for the ClO_4^-. Chloride anions also caused hysteresis, while ClO_4^- didn't and moreover, Cl^- caused surface changes and corrosion. These two phenomena were explained by formation of the AgCl adlayer. Corrosion processes induced by ionic and organic adsorption at electrode surfaces are described more detailed in this literature [78, 79].

Underpotential deposition (UPD) - is a phenomenon of electrodeposition of substances (typically metal cation M to a solid metal) at a potential less negative than the Nernst potential. The UPD is interpreted as a result of an interaction between the deposited metal M and the substrate S (elec-

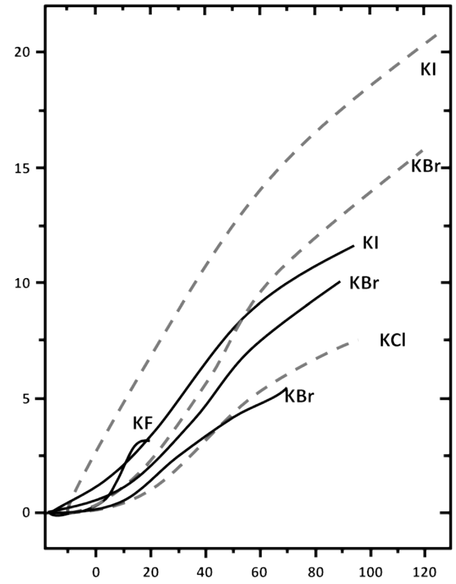

Fig. (8). $\Delta R/R$ vs. surface charge density σ^X for gold (—) and silver (- - -) layer electrodes contacting different potassium halides. The same concentration for the different halides: 0.04 M. σ^X values were extracted from capacitance vs. E curves for different halides. Film thickness: 25 nm. Redrawn from reference [79].

trode). The M-S interaction must be energetically preferred to the M-M interaction in the crystal lattice of the pure metal M. This mechanism was derived from the observation that UPD typically occurs only up to one or two monolayers of the deposited metal M. Underpotential deposition is much more pronounced at monocrystalline than on polycrystalline materials [80].

Molecular adsorption on metal films - As described in the previous sections adsorption of molecules on the thin film metal surface may change the electric resistance of the film. Sensors based on this phenomenon are finding their applications in the gas and liquid phase analysis.

Adsorption of sulphur organic compounds – Cationic surfaces of many transition metals are weak electron acceptors, and show great affinity to weak electron pair donors, such as thiols, disulphides and thioethers. All of these groups have high adsorption energies with respect to metal surfaces - typically in the range of 40 – 50kJ mol^{-1}. This represents about 50% of the energy of the C-C bond. Alkyl derivates of these groups exhibit tendencies to form *self-assembled monolayers* (SAM), with various packing densities. Molecules with chain length >10 carbons are forming high density SAMs with well oriented arrangement [37, 81, 82]. Shorter thiols also assemble, but are not so densely packed and ordered and have lower stability. All alkane-1-thiol SAMs show hydrophobic surfaces with contact angles higher than 100 degrees [83,84]. Omega - substituted (OH, COOH,..) alkane-1-thiols are frequently used as SAM linkers for covalent coupling in biochemistry applications. Formation of the SAM from ethanolic solutions at concentrations of 1–5mM has two phases, in the first, few minutes after immersion the initial, not well ordered layer is formed, followed by relatively slow rearrangement of this SAM in 8-24 h. Longer times don't lead to any measurable improvement in the SAM arrangement [32, 35, 85-88]. An important factor limiting the selectivity of the detection of thiolated species was published [85], showing that during adsorption of 1-alkanethiols of various lengths, the resistivity rises ~ 4% during the full coverage from clear substrate, but for alkyl chain length in the interval of 2 to 16 carbons the increment in resistivity is practically independent on the chain length. However, as confirmed by simultaneous measurements of the film resistance and SPR angle it does depend on molecular character of the adsorbed molecules. Alkanethiol layers do not show much long term stability, when exposed to buffer solution such as PBS, but addiction of anti-oxidants into buffer substantially improves their stability [89]. Aromatic thiol compounds such as 1,4-benzenedimethanethiol (BDMT) or benzenethiol do not exhibit such high rise of resistivity and reach final value of about ¾ of alkanethiol shift [88]. Aromatic thiols also form SAMs, which can be used for organic thin film-based electronic devices or sensors [90]. Other important thiolated compounds such as thiolated DNA, cysteine and its derivates and/or glutathione also bind to metal surfaces such as Au or Ag and are frequently used for derivatization of nanoparticles [91-94]. Additional interesting substances, which can be adsorbed at the gold surface include conducting polymers such as the poly(o-aminophenol) (POAP), which can change the specularity parameter of the thin metal film and subsequently its conductivity depending on its oxidation state [95-97].

CONCLUSION AND FUTURE PROSPECTS

This short overview was focused on technologies for preparation and potential analytical applications of thin metal films with direct resistivity measurement. At present the main application area of such sensors lays in gas sensing. The use of chemiresistors for sensing in liquids, and especially in water solutions is much less developed. Liquid phase thin metal film sensors are currently dominated by optical and/or electrochemical detection; however, the instrumental simplicity of resistivity measurements is very attractive and new developments in this area can be expected in the future.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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ABBREVIATIONS

α_ρ = temperature coefficient of resistivity

α_R = temperature coefficient of resistance

α_T = thermal expansion coefficient

λ = mean free electron path

v = the velocity of the electron

τ = the collision time

$\hbar k$ = the de Broglie's momentum of a quantum wave

m = mass of the electron

$\Delta G/G$ = relative change in the conductivity

N_e = surface density of induced free electrons

N_a = surface density of adsorbed species

x' = proportionality constant

p = specularity parameter at metal / analyte interface

p' = specularity parameter at metal / substrate interface

θ = angle of incidence

ρ_0 = temperature coefficient of resistance at standard temperature

ρ = temperature coefficient of resistance

T = temperature

T_{ads} = adsorbate surface concentration

p = specularity parameter

Δp = specularity parameter change

k_1 = proportionality constant between specularity parameter change and surface concentration of adsorbed specie

ρ_b = surface resistivity of bulk metal

ρ_f = surface resistivity of thin film electrode

$\Delta\rho_f$ = surface resistivity change of thin film electrode

l_0 = mean free path of conduction electrons

d = film thickness

Δd = film thickness change

K_0 = proportionality constant between resistivity change and surface concentration of adsorbed specie

$T_{ads.lim}$ = limiting value of surface coverage

σ^X = surface charge density

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