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COATINGS FOR MICROIONIC DEVICES

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Résumé - Le concept de microionique désigne la transposition des procédés de fabrication de la microélectronique à des dispositifs électro-chimiques. Après quelques exemples de dispositifs, sont exposées des méthodes de réalisation de couches minces et épaisse.

Abstract - The concept of microionics designates the transposition to the field of electrochemistry of the methods which made possible the spreading of the microelectronics. Some examples are shown, and methods of making thin and thick films are reviewed.

I - INTRODUCTION

In the tremendous advances in integrated electronics one main factor has been the improvement of thin and thick film technology. Miniaturization and high integration have many advantages: low energy consumption, collective manufacturing, reliability, low cost. Velasco created the concept of microionics to qualify the methods used in the production of microelectronics transposed to the domain of ionic solid state.

Microionics concern hybrid, thick and thin film technologies, because it uses different materials for different functions. Nevertheless it is conceivable in some cases to modify the characteristics of ionic materials by doping to make monolithic circuits. For example, ceria doped with some per cent of calcia or yttria is an ionic conductor, and doped with tantalum or niobium oxide it is an electronic conductor, so it is possible to imagine monolithic cells made only with doped ceria.

The transposition of the methods of the microelectronics to the ionic materials domain is difficult, because ionic materials are generally polycrystalline, with complex structures and compositions, and because interfacial phenomena still poorly understood are often limiting kinetically. However, this may sometimes turn in a benefit. Two review papers give details on these topics /1,2/.

II - EXAMPLES OF MICROIONIC DEVICES.

ISFETs and CHEMFET sensors

Ion-sensitive field effect transistors (ISFET) and chemically sensitive field effect transistors (CHEMFET) are field effect transistors in which the field is created by net electron or ion transfer at electrolyte-metal and electrolyte-ion exchanger interfaces because of space charge generation /3...10/. The isfet device is generally operated without any reference electrode in the liquid, i.e. in the floating "virtual...
Hybrid technology can lead to pH and Ca sensitive electrodes in which the Nernst potential generated across a selective membrane (PVC doped with an ion-exchange salt) is applied to a source-follower FET. An inner reference material is applied to the conducting strip before forming the membrane.

Resistive sensors

Several thin film cells are sensitive to reducible or oxdizing gases, dependant on defect equilibrium processes of the electrolyte with the atmosphere, or on electrode kinetics. For example are LaF₃, CeF₃ or PbF₂ cells sensitive to O₂, CO, SO₂, NO₂ and NO. /28, 29, 30/.

Potentiometric sensors

Potentiometric sensors with a reference electrode can be made in microionic solid state. As an example, Velasco made an hydrogen microsensor with a planar structure with HUP (Hydrogen Uranyl Phosphate) as an electrolyte, and a metallic hydride as a reference electrode /31/. Zirconia potentiometric sensors with conventional ceramic structure are well known, and attempts are made to make them with thick film /32, 33, 34/, thin film or mixed structure /31/. The main use of such sensors is the control of engine exhaust gas, and they work as classical "lambda" sensors. But lambda sensors can only monitor air/fuel ratio at the stoichiometric value, and are poisoned by lead. An other design with a catalic diffusion path seems to clean the leaded gas. Somewhere between this diffusion path and the oxygen concentration cell, an electrochemical pump based on a zirconia membrane can be added, which is used for injecting or removing oxygen from the tested gas fraction. Then the titration curve is translated quantitatively depending on the electrochemical pump current.

Galvanic cell

The concept of decreasing the cell resistance by using thin film electrolytes has been invoked /13/. However these devices exhibit a high resistance due to the electrode-electrolyte interfaces. The main advantages of thin film cells are the ability to fabricate large electrode areas easily and to make miniaturized batteries which could complement other miniaturized electronic devices.

One of the earliest thin film galvanic cells to draw significant currents reported by Yamamoto and Takahashi /15,20/ was of the type Ag/Ag₃SI/I₂,C. Berger has patented other silver-based thin film cells for use in microelectronic integrated circuits, with RbAg₄I₅, Ag₃SI, Ag₇I₄PO₄ and Ag₄SH₄I₄ as electrolytes /16,17,18/). The thick film technique was used by Ervin to prepare cells of the type Ag/RbAg₄I₅/Rb₂TeI₆ /19/. Other examples are lithium iodide /21, 22/ or lead fluoride /23/ cells.

Coulometers

Coulometers and timers do not require extremely high conductivity or energy storage. Films offer the possibility of cell arrays in which multiple timing or integrations can be accomplished. An electrolytic coulometer tabulates coulombs of charge by plating a metal (or chemical compound) on an inert indicator electrode. A typical example is a cell consisting of a gold indicator electrode and a silver counterelectrode separated by a solid electrolyte containing silver ions. Solid electrolytes investigated include AgBr /24/, RbAg₄I₅ /25,26/, Ag₁₉I₁₅P₂O₇ /27/.

Electrochromic displays

Electrochromism is a colour change induced in a material by an applied electric field or current. It was proposed for application in information displays by Dreyer /37/. Many electrochromic cells which consist of thin or thick films have been patented. The most widely studied material is WO₃ which is sandwiched between two electrodes /38, 39, 40/ or between electrode and electrolyte /34/. Similar effects were found for MoO₃ /4/.
Another electrochromic cell uses as a substrate the ceramic fast-ion conductor cationic beta-alumina, (the cation being lithium, sodium or potassium), all the other components are deposited in thin film form /43/.

Fig. 1: Idealized layouts for Isfets and Chemfets sensors. Fets may be n- or p-type. An SiO2 gate and an AgBr sensor membrane are used in these examples. Other ion-exchanging membranes, surface coatings, or layers can be used to enhance specific adsorption (After Bick /4/ and Shemb /5/).

Fig. 2: Basic structure of an hybrid selective electrode. An inner reference material is applied to the conducting strip before applying the PVC membrane doped with an ion-exchange salt (After Afromowitz 5 coll. /11/).

Fig. 3: A rechargeable solid electrolyte battery composed entirely of evaporated films proposed by Mogudish /14/, and a thin film twelve-cell coulometer configuration after Kennedy & Chen /24/.
**Fig. 4:** A planar thin film hydrogen-gas sensor and its electrical response after Velasco & coll. /31/, and a thick film zirconia oxygen sensor including heating element after Nissan Hot. Cy /35/.

**Fig. 5:** Lambda sensor with thin and thick films, and its response (up), and combustion sensor with pumping current (down). (reference electrode= Pd/PdO, 700 C, synthetic atmosphere O2 18%, CO2 10%, N2, CO var.) after Velasco & coll. /31/. 

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- **Hydrogen sensor**
  - E.M.F. (mV) vs. \( P_{H_2} \) (ATM)
  - \( T = 24^\circ C \)
  - Pd/HUP/Pl (H2 - N2)
  - Insulation layer
  - **C.S.Z.** thin film \( \approx 2\mu m \) thick
  - Pt porous thick film \( \approx 15\mu m \) thick
  - Pd/PdOx thick films \( \approx 20\mu m \) thick
  - Enamel protection
  - Lean -> Rich
  - Electrolyte = Pd/PdO, 700 C, synthetic atmosphere O2 18%, CO2 10%, N2, CO var.

- **Sapphire substrate**
  - Porous platinum
  - Porous zirconia electrolyte
  - Enamel protection
  - Contact layer
  - Metal/Metal oxide reference electrode

- **Graphs**
  - Sloiosthermolgy
  - mV vs. % CO
  - Current: I = 0.4A, I = 2A, I = 6A
III - PREPARATION OF THIN AND THICK FILMS

Chemical vapour deposition (C.V.D.).

A material may be plated from a vapour if it forms a volatile compound which can readily be dissociated below the melting point of the material. C.V.D. is one of the most important techniques for the semi-conductor industry and corrosion protection.

The kinetics of reactive film preparation is a complex multi-barrier problem. However, reactive film preparation does work reliably, with better epitaxial growth than with purely physical methods. This is explained by the activating effect of chemical reactions; the alteration of chemical bonds at the surface region causes sufficient mobility for proper readjustment of the particles in the growing film.

For zirconia the chemical vapour deposition is obtained by feeding ZrCl₄ vapour into an O₂/H₂ flame /44/. HfO₂ and ZrO₂ films can be deposited by the oxygen-assisted decomposition of hafnium β-diketonates at temperatures in the range 400-500 °C. Films obtained are fine-grained and close to stoichiometry /45,46/.

Parameters as gas flow, gas composition, geometry of the reaction chamber, substrate temperature... are adjusted empirically.

Spraying and Pyrolysis

Another method for metallic oxides is based on the thermal decomposition of an aerosol obtained by conventional spraying /50/ or by ultrasonic spraying /48,49/ of a solution of a metallic salt or of an organo-metallic compound (tetrachloride, acetylacetonate, ...) on a substrate at a temperature around 500 or 600 °C. This method only differs from classical C.V.D. by the transport mode of the reactive but can be applied to blendings. It is a low cost process which can be applied to prepare a wide variety of complex compounds.

Vacuum evaporation

The material is vaporized and condensed on the substrate surface in a vacuum sufficient to prevent collision between the film-forming atoms and residual gas atoms. Thus the vacuum deposition process involves atoms having thermal energies (0.1...0.5 eV) and line-of-sight deposition. To avoid contamination of the deposit, suitable support materials for evaporation sources are refractory metals and oxides. Further selection is made by considering the possibilities of alloying and chemical reactions between the support and evaporant materials. Resistively heated vaporization sources are normally used for low temperature materials, and electron-beam heated sources are used to vaporize refractory materials without pollution.

Some problems arise from incongruent evaporation of compounds: the constituents present in the solid or liquid state differ in vapour pressure, so the composition of the condensate is not the same as that of the source material. In particular, many oxides (Al₂O₃, BaO, Bi₂O₃, NiO, SnO₂, TiO₂, ZrO₂, Ce₂O₃...) when heated in vacuum or sometimes even in air dissociate to their lower oxides. Moreover, solid solutions are modified in composition. Compositional changes can be predicted from thermodynamics, but in practice, empirical information is the most reliable guide in determining the experimental conditions necessary to produce films of the desired composition.

Some other special techniques as reactive, multi-source, and flash evaporation have been developed for compounds:

In reactive evaporation relatively high oxygen pressures (10⁻⁵ to 10⁻² torrs) are deliberately maintained to produce fully oxidized metal films /56/. For example, Bi₂O₃ (yellow in bulk), is in vacuum deposited film found to be shiny and blackish, in contrast to the transparent films obtained by evaporating with oxygen pressure of 10⁻⁴ torrs, or by oxidizing bismuth films in air /53,54/.
The setting of two or more sources in the same evaporation system is widely practiced to produce multilayer films. By operating two sources simultaneously multiconstituent films can be deposited. To avoid cross contamination, the sources must be separated by shields. It is possible to codeposit materials which form neither compounds nor solid solutions. An important example is cermet, whose multiphase nature becomes apparent only after annealing and recrystallization. The main problem in this technique is to control the condensation rates ratio.

An other method is an electron beam which jumps between two or more crucibles.

Flash evaporation is a fast volatilization of finely divided particles falling on the overheated evaporator. Then the less volatile material evaporates without fractionation.

Vacuum evaporation has been used for RbAg$_4$I$_5$ (22,34), Ag$_{19}$I$_{15}$ P$_2$O$_7$ (23,24), Li$_3$N (9), AgI (72,73), AgBr (21,73), PbF$_2$ (20,74,75), LaF$_3$ (25), PbSnF$_4$ (76).

Ion implantation

Recently a method called "ion implantation" has been developed based on the study of ion collisions. The condensation probability of ions depends on their energy. It is close to unity in the range of thermal energies but decreases with increasing energy values. Moreover it can acquire negative values (sputtering effects). Ions with a sufficiently high energy can penetrate into the specimen, and are implanted.

An other method is the field emission deposition (ioncote process, or FED). (52). A blunt wetted needle is used to generate a coating spray of ions and droplets under the action of a high electric field (H.T. typically 12 kV). Coatings of a variety of elements and alloys can be produced in this way, with droplet diameter about 2 μm.

Sputtering

In the sputtering process high energy particles (generally positive gas ions) striking a surface cause the ejection of atoms by momentum transfer. Due to the high energy of the sputtered atoms (1-100 eV), sputter-deposited films have generally better adhesion than vacuum-deposited ones.

The more simple way to generate the positive ions for sputtering is to establish a glow discharge by setting up a high potential between two flat parallel electrodes in a low pressure gas (10$^{-3}$ to 1 torr).

When the pressure is lowered, the glow goes out and sputtering stops. But sputtering at lower pressures should be interesting, to low gas trapped in the film, and to improve the adhesion because of the higher energy of the sputtered atoms when they reach the substrate.

In order to sustain the discharge, the ionization can be increased by injecting electrons from a source other than the target cathode. The simplest method is the use of a hot filament (triod process).

High frequency electromagnetic radiation can excite a discharge in a gas even without any electrodes in the system. The radio-frequency power can be applied by a coil but is generally fed directly to the cathode, superposed on the D.C. bias.

When the target material is an insulator, the charge on the surface cannot be neutralized, and most of the field is concentrated across the insulator. If the dielectric target is mounted onto a conducting plate to which a high frequency power is applied, the target positive charge is neutralized by plasma electrons during the half of the cycle when the target is positively charged.

An other method is the neutralization of the ion beam. Neutralization in this context means that enough electrons are added to obtain electrical neutrality, and does not imply a beam of ground state atoms. The neutralization removes all macroscopic electric fields from the substrate (83).
An important point in the sputtering process is that the chemical composition of a condensed film will often be the same that of the cathode from which it was sputtered.

Reactive gas may be deliberately added to the sputtering system to produce compounds in thin film form.

Sputtering was used for $\text{Ag}_{19}\text{I}_{15}\text{P}_{2}\text{O}_{7}$/77/, $\text{Na}_{3}\text{Ga}_{2}\text{O}_{3}$/78/, $\text{Na}_{2}\text{Al}_{2}\text{O}_{3}$/79/, $\text{ZrO}_{2}$/80,81/, $\text{CeO}_{2}$/84/.

Further improvements may be realized by the combination of two or more methods. Ion evaporation combines low energy ion implantation and thermal evaporation. Ion plating combines evaporation with cathode sputtering/51,57,58,69/: using an evaporation source with an electron beam gun, r.f. ion plating is carried out in the material discharge atmosphere without introducing any gas.

**Fig. 6**: A schematic representation of the experimental arrangement for:
- a) High rate evaporation with dual sources electron beam heating after Kumar & Coll./54/,
- b) Activated reactive evaporation, after Bunsah & Schramm/56/.

**Fig. 7**: The schematic arrangement for ion evaporation (left, after Glaser & Coll./56/), and for ion-plating deposition (right, after Chevallier/69/).
Screen printing

Thick film circuitry became a significant part of the market for microelectronics. Thick film circuits are made by successive operations of screen printing, drying and firing. A wide range of conductive dispersions is now commercially available, including platinum and palladium based inks, so we should be concerned here mainly by electrolytical inks and specially zirconia inks.

The dispersions have to be formulated to give good screen printing properties and are generally a mixture of a glass powder, an active powder (pigment), and a vehicle. The glass gives cohesive properties, the pigment controls the conductive or dielectric properties, and the vehicle is used to control the viscosity during printing.
About the same processing steps are used to produce all the thick films. The dispersion is forced by the action of a squeegee through a stainless steel screen, which bears the pattern to be generated, to a substrate. The printed pattern is dried to remove the vehicle volatile solvents and then fired in an oxidizing atmosphere. The residual organic binders are burnt off and the glassy powder melted to a coherent film, binding the pigment to the substrate.

![Diagram](squeegee)  
*Fig. 10: The principle of the screen-printing with a thixotropic paste.*

The organic part of the paste has a complex rheological role: Without any mechanical solicitation the viscosity must be high to avoid spontaneous pouring through the screen, or to avoid spreading on the substrate after printing. But, during the printing operation, it must be fluid to go through the screen. On the substrate, the viscosity must increase but not too quickly, because a lateral limited flowing due to surface tension attenuates the traces of the lattice of the screen.

The requirements for zirconia films in oxygen sensors besides a good adherence, are pure ionic conductivity and lack of open porosity and cracks: physical or electrochemical diffusion of gases through the zirconia membrane would quickly deteriorate the reference electrode.

On polished alumina the adherence of zirconia is good. On platinum electrodes the binding is weaker, but sufficient if electrodes and electrolyte are co-fired.

Pure ionic conductivity prevents additions of glass powder or other binding materials. The presence of metallic electrodes (platinum) limits the firing temperature and duration.

Chlorides have an influence on the microstructure of the powder and on the sintering /62,63,64/. Commercial powders are composed of agglomerates (0.5 ... 2 microns) of particles whose dimensions are less than 0.2 microns. The highest density agglomerates induce earlier local compaction and porosity when fired. Therefore a dispersion of agglomerates in the screen printable paste is a condition for low porosity /85/.

Another method proposed by Nissan /36/ consists in filling up the pores of a first film by laying on one or several coatings of ink with smaller particles.

The shrinkage during the elimination of the organic vehicle and during firing can reach from 10 to 20 per cent in each dimension. For a screen-printed film on a substrate this retraction must occur only in one direction, perpendicular to the substrate. Prints from the screen can remain on the green film, and initiate fissuring during firing. The solution to this problem lies in optimization of the rheology of the paste.

In spite of these difficulties, it seems to be possible to prepare tight films of zirconia by screen printing.
Plasma spraying

Plasma spraying is a well-established process for thermal-barrier coatings. The powder particles injected into a plasma jet are quickly melted and propelled onto a substrate where they are quenched. The quality of a coating depends mainly on the velocity and temperature of the particles prior to their impact. For successful coatings the feed material must be a free-flowing powder with a particle size range and distribution carefully controlled. Spray powders are usually made by crushing of a fused ceramic followed by selective milling and sizing. Gel process uses as feed material a concentrated dispersion of the ceramic oxide or oxide mixture, which is gelled to the required particle size and shape and then calcined to give the free-flowing oxide particles /59,60,61,83/.

IV - PROVISIONAL CONCLUSION

Microionic technology is only now beginning to be explored. Up to this point we transposed to the microionic domain the methods which were valuable for microelectronics. Materials which are potentially useful for solid state electrochemistry are far more numerous than materials for electronics. For each preparation procedures must be adjusted, taking into account compatibilities with the other materials and requirements for technological homogeneity.

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