Russian Chemical Reviews **62** (3) 237–242 (1993)
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UDC 548.0:612.315.592

Synthesis of thin-layer structures by the ionic layer deposition method

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Abstract. A review is presented of ionic layer deposition, one of the methods of synthesising thin-layer structures of a predetermined composition with very precise thickness control on the surface of a support. Conditions for the synthesis of ultra-thin films of metal oxides, hydroxides, phosphates, chromates, sulphides, and tellurides on the surface of metals, semiconductors, and dielectrics are discussed. The advantages of the method are pointed out, including the possibility of synthesising layers in an automatic regime under mild conditions at room temperature on substrates of complex shape by using simple apparatus. The problems which prevent the wider use of the method are formulated, and ways of solving them are suggested. The bibliography includes 69 references.

I. Introduction

Recent developments in various fields of technology such as submicroelectronics, the production of catalysts and sorbents, and protective coatings have stimulated more demanding requirements for methods of synthesising thin-layer structures. Thus, specific technological problems in the synthesis of thin-layer structures currently being studied include controlling the disposition of different atoms to within one monolayer of the structural units.

This review covers existing methods of high-precision synthesis of thin-layer structures. One of these methods (ionic layer deposition) is examined in greater detail, because it appears to deserve wider recognition from specialists in solid-state surface chemistry.

The methods used to deposit thin layers of solid substances on the surface of various supports can be arbitrarily classified as physical or chemical. The former include methods in which the material to be deposited is evaporated in a vacuum or an inert medium by thermal, electron-beam, cathodic, or magnetron evaporation.[1–5] In the chemical methods the layer is formed by deposition from the gas or the liquid phase as a result of a chemical reaction initiated by thermal energy, by a plasma, by a change in pH, etc.[6,7] A feature common to all these methods is that the layer is formed as a result of a shift in the chemical equilibrium between the reactants in the gas or the liquid phase and the growing layer, in the direction of layer formation. This allows the thickness of the layer to be controlled though the concentration and temperature of the reactants as well as through the temperature of the substrate, the deposition time, and other parameters. However, changes in these parameters do not offer thickness control at the level of a monolayer of structural units.

Essentially new conditions of high-precision layer synthesis have been formulated for the preparation of thin-layer structures: conditions offering an unusual type of chemical assembly.[8–12] The most important of these is a special preparation of the substrate surface. A layer of functional groups is then formed on the prepared surface, and used to induce the chemisorption of bifunctional molecules containing atoms of the layer to be synthesised and of molecules of another reactant, not less than bifunctional, giving new functional groups which contribute to further chemisorption reactions. This removes the excess of reactants. As a result, the direct synthesis is replaced, in the complex conditions created by the thermodynamics of the process, by a stepwise synthesis with acts of irreversible chemisorption alternating in a predetermined sequence.

These ideas have been used in a series of studies[13–17] of the synthesis of various metal oxides (TiO_2, Cr_2O_3, etc.) on the surface of dispersed solids (mainly silica), and also of multizone layers based on these materials. Readily hydrolysed chlorides and water are most commonly used as reactants. The method of synthesis of layers of a single composition has been called molecular layer deposition. Organometallic compounds have also been used for this purpose,[18–21] for example $Ti(OC_2H_5)_4$, $Si(OC_2H_5)_4$, $Al(OC_3H_7)_3$, $Zn(CH_3)_2$, $Cd(CH_3)_2$, H_2S, etc. The advantages of this method include, in addition to a precise control of the layer thickness, the ability to deposit layers on the surface of porous supports having a complex shape.

This approach has been used in conjunction with molecular beam epitaxy[22] to expose the support in an ultra-high vacuum to alternating beams of atoms of different elements which react on the support but not in the gas phase. The method is also used to prepare various thin-layer materials used in microelectronics (for example, $Ga_{1-x}Al_xAs$).

A definite analogy has been reported also with the atomic beam epitaxy method,[23–25] in which a layer of ZnS is deposited on the substrate surface by heating the substrate above the evaporation temperature of both the reactants (in this case, zinc and sulfur), and the chemisorption of zinc and sulfur atoms is

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Received 8th September 1992
Uspekhi Khimii **62** (3) 260–265 (1993); translated by J I Carasso

obtained by successively exposing the surface to these atoms. The method has been used in the synthesis of high-purity layers of ZnS, CdS, ZnSe, CdSe, etc.

These methods require the use of vacuum or high-vacuum apparatus, or flow apparatus filled with a purified inert gas. The molecular layer deposition method has also been used[26] for synthesis experiments in inert solvents.

This interest in the preparation of layers by using liquid reactants is not new, mainly because the apparatus requirements are much simpler for synthesis in the liquid phase. Thus, the impregnation method is now widely used in the development of catalysts and sorbents.[27] An inert matrix is immersed in a solvent containing the substance to be deposited, and (without washing away the excess of reactants) the system is then heated or treated with another reagent which converts the deposited substance into a sparingly soluble compound. This technique infringes one of the fundamental requirements of precision synthesis by failing to remove the excess of reactants.

Evidently, the most stringent control over the synthesis conditions of the layers from the liquid phase can be exercised by using ion exchange reactions, now widely applied for the modification of solids.[28-30] However, the application of ion exchange reactions in the synthesis of thin-layer structures involves serious difficulties, mainly associated with the fact that these reactions are reversible, and therefore the layer produced in the first few layer deposition cycles can be lost in experiments involving repeated depositions.

II. Conditions for the synthesis of thin-layer structures by ionic layer deposition

The layer synthesis from solutions on a substrate surface was first proposed by Iler,[31] who prepared layers of silicon oxide by using charged particles of colloidal silica as the initial structural units for layer deposition. Treating the surface of a substrate carrying a charge opposite to that of the colloidal silica particles resulted in the deposition of a layer of the particles. A subsequent treatment of the substrate and the deposited layer with a salt solution produced charge reversal in the supported particles, with deposition of a second layer.

The application of these ideas to the synthesis of layers with very precise thickness control, with cations and anions used as the main structural building blocks, is complicated first and foremost by the reversibility of the ion exchange reactions taking place on the surface.

Nevertheless it has been shown[32,33] that the silica gel containing PO_4^{3-} as a substituent is an effective sorbent for the Hf^{4+}, Zr^{4+}, and Sn^{4+} ions. It has also been shown[34] that Ca^{2+}-substituted silica gel can be used as an anion exchanger for PO_4^{3-}. An increased adsorption of PO_4^{3-} ions on Zn^{2+}-substituted silica gel (as compared with the H^+-substituted silica gel) has also been reported.[35] It was suggested that one layer of metal phosphate is formed on the surface by the interaction with the solution.

These results can be explained by the well-known Fajans rule:[36] ions are adsorbed most effectively on a surface if they form a sparingly soluble or a weakly dissociated compound with an oppositely charged ion in the substrate.

Thus it may be possible to prepare thin-layer structures by using the principles of the chemical assembly of solid substances, realised by the molecular layer deposition method (which relies on the irreversible adsorption of easily hydrolysed metal chloride molecules). In other words, ions can be used for the synthesis instead of molecules, thus producing an ionic type of layer deposition.

The irreversible adsorption reactions of anions and cations, giving sparingly soluble compounds as a result of the interaction, provide the foundations of the ionic layer deposition method. In this approach the thickness of the layer is determined by the number of cycles of ionic layer deposition performed, including the removal of the excess of reagents between cycles. In this case the support behaves alternately as a cation exchanger and as an anion exchanger, which allows the now well-understood ion exchange concepts to be used. The conditions for the most complete ion exchange and the exchange capacity are well established for almost all the types of ion exchanger: furthermore, the appropriate thermodynamic and kinetic relationships have been obtained, sequences of exchanging ions have been formulated, and reaction mechanisms have been proposed.[37-47]

However, there is as yet no systematic treatment of the basic process involved in the synthesis by the ionic layer formation method (namely, the problem of the conditions for which the ion exchange reactions are irreversible). To some extent this state of affairs is exactly the opposite of the problems encountered in developing effective ion exchangers, since a long operating life in that case requires a knowledge of the reversibility conditions of the adsorption of ions on the surface. Very little is known about the ability of the layers synthesised in the first stages of layer deposition to take part in later ion exchange reactions during repeated exposures of the support to the reactants, and also about the properties of the layers synthesised in this way.

III. Preparation of thin layers of various compounds

Synthesis of manganese oxide and chromium hydroxide layers. At first sight layers of metal hydroxides and oxides can be synthesised by successively depositing layers of metal and of hydroxyl ions on the surface by the scheme

$$[M]OH + M_1^{n+} \rightarrow [M]OM_1^{(n-1)+},$$
$$[M]OM_1^{(n-1)+} + OH^- \rightarrow [M]OM_1(OH)_{(n-1)}.$$

However, this expectation is not fulfilled, since the layer of hydroxide formed after the first cycle redissolves in subsequent exposures to a solution of the metal salt, even at the highest pH values, by the reaction

$$[M]OM_1(OH)_{(n-1)} + H^+ \rightarrow [M]OH + M_1(OH)^+_{(n-1)}.$$

Therefore the writer proposed a method of synthesising hydroxide layers by converting the ions of the adsorbed metal layer into a higher valency state, for which the interaction with the solution of the metal salt is not reversible.[48] Layers of MnO_2 were synthesised in this way from $Mn(NO_3)_2$ or $MnSO_4$ and $KMnO_4$. As a result of these reactions every manganese ion was converted into the Mn^{4+} state of oxidation by the scheme

$$[M]OH + MnOH^+ \rightarrow [M]OMnOH + H^+,$$
$$[M]OMnOH + MnO_4^- \rightarrow [M]O(MnO_2)_2OH.$$

A more substantial adsorption of Mn^{2+} ions on the substrate surface was obtained by adding NaOH to a solution of $MnSO_4$ to give a pH value differing by a few tenths of a pH unit from the $Mn(OH)_2$ precipitation value. After each treatment the excess of reagent was removed by washing the sample with an aqueous solution saturated with Mn^{4+} ions. This suppressed the dissolution of the MnO_2 layer even at the stage of washing the support and its layer free from the excess of each of the reagents.

The synthesised layers were studied spectrophotometrically in the visible and UV regions and by IR spectroscopy. Their composition was found to correspond to hydrated MnO_2, and a regular increase in the layer thickness with the number of layering cycles was demonstrated.

The coating of the surface of carbon steel with a layer of chromium hydroxide has also been reported.[49,50] In this case the support was treated successively, several times, with aqueous solutions of H_2CrO_4, CrO_3, and $Na_2S_2O_3$ or $NaNO_2$, and washed free from the excess of reagent with water after each exposure. Irreversibility of the adsorption of the $HCrO_4^-$ ions on the surface of the growing layer of hydroxide was achieved by an intermediate heating of the substrate bearing a thin layer of CrO_3 solution to

150–200 °C. This heating stage evaporated the water and resulted in binding the $HCrO_4^-$ (for example) to the FeOH groups of the surface by forming Fe–O–Cr groups:

$$[Fe]OH + H_2CrO_4 \xrightarrow{T} [Fe](OCrO_2OH)_{ads}(CrO_3)_x ,$$

$$[Fe](OCrO_2OH)_{ads}(CrO_3)_x \xrightarrow{H_2O} [Fe](OCrO_2OH)_{ads} ,$$

$$[Fe](OCrO_2OH)_{ads} + Red \rightarrow [Fe]OCr(OH)_2 .$$

After this treatment in a reducing solution the adsorbed Cr^{6+} ions were converted into the Cr^{3+} ions of a layer of chromium hydroxide, which is insoluble at the given pH value.

A practically important result of these syntheses is a marked increase in the corrosion resistance of the steel surface, depending on the number of layer deposition cycles. Thus, whereas a repeated treatment with solutions of oxidiser and reducer produces a negligibly small change in the corrosion resistance, an alternating treatment by the ionic layer deposition mechanism gives an almost 15-fold improvement after 10 layer deposition cycles, as shown by measurements in a 2% solution of $CuSO_4$. It is also important to note that the observed corrosion resistance values greatly exceed the level of protection offered by existing methods of depositing chromate conversion coatings.

Synthesis of layers of barium phosphate and zinc chromate. Reference was made above to some studies[32–35] of the increased adsorption of PO_4^{3-} ions on the surface of cation-exchanged forms of silica gel and of metal ions which form sparingly soluble compounds with PO_4^{3-} on the surface of phosphate-substituted silica gel. However, no detailed mechanism of these interactions has yet been suggested.

A recent Patent[51] discloses a method of synthesising a layer of barium phosphate on a carbon steel surface by using $Ba(NO_3)_2$ and Na_2HPO_4 as reagents with an intermediate washing of the sample with water to remove the excess reactants and products:

$$[Fe]OH + Ba^{2+} \rightarrow [Fe]OBa^+ ,$$

$$[Fe]OBa^+ + HPO_4^{2-} \rightarrow [Fe]OBaHPO_4^- .$$

A result of practical value from this work was the achievement of an almost 10-fold increase in the corrosion resistance of the metal as compared with the existing method of producing phosphate conversion layers. This difference can probably be ascribed to a lower porosity of the coatings obtained by the new method.

Great interest has been shown in the synthesis of binary oxide layers not only on pure metal surfaces but also on a metal coated with a layer of oxide prepared (for example) by a passivation treatment. In this case we have shown[52] that a synthesis by the ionic layer deposition of $ZnCrO_4$ on a layer of the same compound on zinc (obtained in a passivating chromate solution) produces a greatly increased corrosion resistance of the surface after 10 layer deposition cycles, and solves the practically important problem of increasing to 200 °C the thermal stability of the passivating conversion layer, which had a limit of 60 °C before the layer deposition treatment. The reagents used in this study were $Zn(CH_3COO)_2$ and Na_2CrO_4. Irreversibility of the adsorption of CrO_4^{2-} on the $ZnCrO_4$ surface was achieved by an intermediate heating of the sample with a layer of Na_2CrO_4 solution at 150–200 °C for 1–2 min:

$$[Zn](ZnCrO_4)_mZnOH + Na_2CrO_4 \xrightarrow{T} \rightarrow [Zn](ZnCrO_4)_m(ZnCrO_4^-)(Na_2CrO_4)_x ,$$

$$[Zn](ZnCrO_4)_m(ZnCrO_4^-)(Na_2CrO_4)_x \rightarrow \rightarrow [Zn](ZnCrO_4)_m(ZnCrO_4^-)_{ads} ,$$

$$[Zn](ZnCrO_4)_m(ZnCrO_4^-)_{ads} + Zn(CH_3COO)_2 \rightarrow \rightarrow [Zn](ZnCrO_4)_m(ZnCrO_4)Zn^+_{ads} .$$

Synthesis of layers of copper and zinc sulphides. The first studies of the synthesis of ultra-thin layers of CuS were carried out by the method proposed by Rotrekl et al.[53] in the early 1970s. The method has been developed for the deposition of an electrically conducting layer on the surface of a dielectric. These layers are strongly bound (chemically) to the surface, and their electrical resistance is relatively low. Therefore they produce effective current-carrying layers for the electrochemical metallisation of dielectrics (and especially of plastics). Published work in this area has already been reviewed.[54]

In most cases the layers of CuS were synthesised by using solutions of $CuSO_4$ and Na_2S as reagents. When a layer is deposited on supports made of various materials (wood, fibrous silicates, unglazed porcelain) the first stage can be the adsorption of either Cu^{2+} or S^{2-} ions. To increase the thickness of the deposited layer the substrate should be washed free from the excess of Cu^{2+} with hot water, which hydrolyses the surface compounds of Cu^{2+} and inhibits their removal. In treatments by 3–5 exposures the sample is not usually washed free from the excess of S^{2-} ions: this also favours the deposition of thicker layers. In this way the resistance of a layer of CuS was lowered to 10^3–10^4 Ω cm^{-1} after three treatments. Even lower resistances have been obtained[56] by adding Zn^{2+} ions to the solution of $CuSO_4$.

All these studies had one feature in common: they aimed to solve a specific technological problem (in this case, the production of an electrically conducting layer). Little attention was paid to the special aspects of the synthesis or to the mechanism of the reactions.

These problems were adequately studied (in the case of ZnS and CdS layers) by Nikolau et al.,[56–60] who proposed the term SILAR (Successive Ionic-Layer Adsorption and Reaction) for the above method of synthesising metal sulphide layers. Other names have been used for the same procedure in the Russian literature: ionic layer epitaxy[61] and layer chemisorption.[62] We believe that all these names only partially reflect the true nature of the processes taking place on the surface, since the ionic layer deposition may not involve epitaxy, and the dominant process in the synthesis could be the interaction of layers of physisorbed ions. In this review we shall retain the term which has been adopted in the Russian literature, and call the process (by analogy with molecular layer deposition) ionic layer deposition. This term is only slightly different from the term proposed by Nikolau.

It has been established[56] that in the synthesis of a layer of ZnS on the surface of ITO the maximum growth rate (3.0–3.1 Å per cycle of layer deposition) is obtained by using a 5 M solution of $ZnCl_2$ and a 2.8 M solution of Na_2S. For CdS the maximum rate of 1.3–1.4 Å per cycle was obtained for a 5 M solution of $CdCl_2$ and a 2.8 M solution of Na_2S. The maximum surface coverages during the adsorption were calculated from the growth rates: $\Phi_{Zn} = 0.72$ and $\Phi_S = 0.72$ (for ZnS) and $\Phi_{Cd} = 0.23$ and $\Phi_S = 0.2$ (for CdS).

In order to identify the mechanism of the adsorption of Zn^{2+}, Cd^{2+}, and S^{2-} the ξ potentials were measured[58] in solutions of different concentrations and different pH. Three critical points were found on the experimental curves: CR1, CR2, and CR3. At pH values lower than CR1 (2.3 for ZnS and 1.8 for CdS) the sulphide surface is positively charged owing to the adsorption of H^+ on the sulfur adsorption centres. For pH values between CR1 and CR2 (up to 7.5 for ZnS and up to 10 for CdS) the charge can be both negative (because of the ionisation of Brönsted-acid centres) and positive (because of the adsorption of the Zn^{2+} and Cd^{2+} ions on these centres or of the chemisorption of $ZnOH^+$ on the S^{2-} ions). At pH > 9 for ZnS and pH > 11 for CdS the surface is charged negatively because of the adsorption of OH^- ions on $Zn(OH)_2$ and $Cd(OH)_2$.

If one allows for these results and for data on the growth rate of layers in solutions of reagents of different concentrations, the following model can be proposed for the growth of the layer.

As we know, the dissolution of $ZnSO_4$ and Na_2S in water is accompanied by dissociation and hydrolysis:

$$ZnSO_{4\,aq} \leftrightarrows Zn^{2+}_{aq} + SO^{2-}_{4\,aq},$$
$$Zn^{2+}_{aq} + H_2O \leftrightarrows ZnOH^{+}_{aq} + H^{+}_{aq},$$
$$Na_2S \leftrightarrows 2Na^{+}_{aq} + S^{2-}_{aq},$$
$$S^{2-}_{aq} + H_2O \overset{(HS^-)}{\rightleftharpoons} HS^{-}_{aq} + OH_{aq}.$$

As soon as the ZnS support is immersed in a solution of $ZnSO_4$ the Zn^{2+} and $ZnOH^+$ ions react with the HS^-_{ads} to form more ZnS:

$$Zn^{2+}_{aq} + HS^{-}_{ads} \rightarrow ZnS + H^{+}_{aq},$$
$$ZnOH^{+}_{aq} + HS^{-}_{ads} \rightarrow ZnS_{ads} + H_2O.$$

Under these conditions only the number of zinc ions determined by the number of adsorption centres on the surface is taken up by the substrate, and the synthesis takes place under the condition

$$[HS^{-}_{ads}] \geqslant \frac{SP_{ZnS} K_1 [H^+]}{[Zn^{2+}_{aq}]},$$

where SP ($\cong 2 \times 10^{-22}$) is the solubility product of ZnS and K_1 ($\cong 1 \times 10^{-15}$) is the protonation constant of S^{2-}. The following condition must also be fulfilled in order to avoid layer formation by the precipitation of colloidal ZnS:

$$[HS^{-}_{aq}] < \frac{SP_{ZnS} K_1 [H^{+}_{aq}]}{[Zn^{2+}_{aq}]}.$$

Beyond this point we find a superequivalent adsorption of Zn^{2+} and $ZnOH^+$ on the ZnS, and the charge on the surface becomes positive.

When the substrate is washed in distilled water some of the zinc ions are removed from the surface, but the pH at the surface is changed to 7 by the water, causing hydrolysis of the zinc ions which opposes the desorption.

If the substrate is then immersed in a solution of Na_2S, the S^{2-} and HS^- ions react on the surface, giving a layer of ZnS:

$$Zn^{2+}_{ads} + S^{2-}_{aq} \rightarrow ZnS,$$
$$ZnOH_{ads} + HS^{-} \rightarrow ZnS + H_2O.$$

Because of their higher mobility the OH^- ions can reach the surface more rapidly when $[S^{2-}] = [OH^-]$, and react with formation of $Zn(OH)_2$. However, since the solubility product of $Zn(OH)_2$ (1.2×10^{-17}) is much greater than that of ZnS, the first formations are rapidly converted into ZnS and the positive surface charge disappears. The layer of ZnS is formed when the following condition is satisfied:

$$[Zn^{2+}_{ads}] \geqslant \frac{SP_{ZnS} K_1 [H^{+}_{aq}]}{[HS^{-}_{aq}]}.$$

To avoid the precipitation of colloidal particles of ZnS we also require that

$$[Zn^{2+}_{aq}] < \frac{SP_{ZnS} K_1 [H^{+}_{aq}]}{[HS^{-}_{aq}]}.$$

Thus the complete synthesis includes several different stages of diffusion and adsorption of ions.

As can be seen from the above description of the ionic layer deposition mechanism it should be possible to dope the layer with various ions and to create a distribution of the doping impurity over the thickness of the layer by exposing the substrate to solutions of various salts. This approach has been used in a study[59] of the synthesis of electroluminescent layers of ZnS and CdS doped with indium and manganese incorporated into the structure of the layer from solutions of $InCl_3$ and $KMnO_4$.

Layers of ZnS and CdS have also been produced[61-63] by using silicon and germanium in the (111) orientation as substrates and $Zn(NO_3)_2$, $Cd(NO_3)_2$, and Na_2S as reagents. Solid solutions of $Zn_{1-x}Cd_xS$ were synthesised from mixed aqueous solutions of $Zn(NO_3)_2$ and $Cd(NO_3)_2$.

The resulting layers, up to 200 nm thick, had a smooth mirror-like surface; the layer thickness produced by one layer deposition cycle was 3.2 Å for ZnS and 2.9 Å for CdS, corresponding to ~90% coverage of the surface by adsorbed ions.

Electron-diffraction studies of these materials showed that for ZnS the growth of the layer on the substrate surface begins with the formation of crystallites having a lattice of the wurtzite type, but when the layer thickness is increased (after 30–40 cycles) polycrystallites begin to grow with a lattice of the sphalerite type. The growth of CdS on Si(111) begins with the formation of a polycrystalline cubic structure, in which some of the crystallites are oriented in the (111) plane as the layer thickness is increased. On the other hand $Zn_{1-x}Cd_xS$ solid solutions are obtained only when the mole fraction of Cd in the solution is 0.0001–0.003, the most perfect layers being formed for $x = 0.0002$. When $x = 0.003$ the structure of the layer corresponds to the CdS cubic lattice.

Kutepov et al.[63] have studied the effect of the concentration and temperature of the solutions on the refractive index of the ZnS layers. It was established that the lowest density is found in layers grown from concentrated solutions and from solutions with identical concentrations of the reactants but prepared at low temperatures, and also in layers synthesised from the most dilute solutions. The highest refractive index was observed for solutions with a 5-fold excess of the concentration of $Zn(NO_3)_2$ over the concentration of Na_2S and at high temperatures.

In addition to ZnS, CdS, and $Zn_{1-x}Cd_xS$, layers of PbS have been synthesised by using aqueous solutions of $Pb(CH_3COO)_2$ and Na_2S as reagents on a Si(111) surface. These layers had a mirror-smooth surface and were strongly held on the substrate. After 100–200 deposition cycles their thickness was 30–50 nm, corresponding to a growth rate close to a monolayer per cycle. The structure of the PbS layers was assigned to the block monocrystal type, with a small disorientation of the blocks and a block size of 0.1 μm.

Klechkovskaya et al.[62] explained published results[56-63] on the growth mechanism of sulfide layers by postulating that the lattice parameters and the structural parameters of the substrate play a dominant role in the formation of the structure of the growing film (especially during the first stages of layer deposition). However, it was noted that under the conditions of the experiments the ordinary growth mechanism is predominant, including the adsorption of ions of both components, the formation of three-dimensional growth centres (which are not oriented with respect to the substrate in the initial stages when the mismatch of the lattice parameters is large), and their coalescence with a preferred orientation and the subsequent growth of a new layer on the substrate surface.

The growth mechanism suggested[61,63] for metal sulfide layers differs from the mechanism proposed by Nikolau,[58] probably because of the nature of the substrate materials. Thus, the former workers[61-63] used silicon and germanium as substrates, whereas Nikolau[58] used mainly ITO and molyb-denum, which adsorb S^{2-} ions as well as incorporating them in the structure of the layer growing on their surface. On the other hand when silicon or germanium are used as substrates allowance must be made for the reversibility of the adsorption of the Zn^{2+} and Cd^{2+} ions on SiOH and GeOH. Thus it has been shown[64] that in the adsorption of salts of these metals from aqueous solutions monolayer coverage of the surface by OH groups does not take place, and that when the sample is subsequently washed free from the excess of reagents the metal in the Si–O–M bond is replaced by a proton. Clearly, the first treatments do not form continuous layers of the sulfides on the surface. We must also allow for the possible adsorption, from solutions of metal salts at concentrations greater than

0.01–0.001 M, of clusters of metal hydroxides, formed (as reported[65–67]) during the ageing of the solutions. The subsequent treatment of these layers in a solution of sodium sulfide, which has a strongly alkaline reaction, should produce a partial dissolution of the hydroxides with precipitation of the sulfides by the destructive epitaxial interaction mechanism. Under these conditions a continuous layer cannot be produced during the initial stages of the treatment. A possible explanation of the mechanism of the three-dimensional growth of the layer may be found in the suggested[68] superequivalent adsorption of the ions on the surface at solution concentrations greater than 0.001 M.

A substantial contribution to the uncontrolled growth of the layer comes also from the incomplete removal of the excess of reagents from the substrate. In this case the thickness of the prepared layer is determined by the kinetic parameters of the washing operation. In spite of its importance this topic is not adequately dealt with in published papers.[56–63]

Synthesis of layers of cadmium telluride on a gold electrode surface. It has been pointed out[57] that the ionic layer deposition method can be used to synthesise layers on electrode surfaces by controlling the adsorption processes through the electric field. Clearly, the ions which interact on the surface have a charge, and their motion can therefore be controlled by an electric field.

Thus, Shtikin et al.[69] deposited, in a thin-walled electrochemical cell, two monolayers of CdTe on the surface of a gold single crystal which had been previously cleaned in an ultra-high vacuum. The reagents were a 1.0 μM solution of $CdSO_4$ in an acetate buffer and a 0.4 μM solution of TeO_2 in H_2SO_4 (pH 2.2). The potential of the electrode was varied between −0.6 and 0.8 V at a rate of 2 mV s^{-1} while measuring the current in the cell filled with each reagent successively. Two peaks, corresponding to the adsorption of the Cd^{2+} and the Te^{2-} ions, were detected in the current–voltage curves.

The composition of these layers was studied by low-energy electron diffraction and Auger spectroscopy, and a structure-chemical model of the arrangement of the atoms in the layer was constructed. This suggested a high degree of perfection of the layers and good control over the conditions of synthesis.

IV. Conclusions

The experimental information reviewed above makes clear several advantages of the ionic layer deposition method, such as the possibility of depositing layers of various substances (including pure substances and multicomponent binary compounds of the main classes of solids), the high precision of control over the layer thickness, and the ability to prepare layers in automated regimes at low temperatures on objects of complex shape. In spite of the simplicity of the method, the synthesis of a layer on the surface relies on several processes in parallel: the adsorption and desorption of the ions, their multistage hydrolysis, and diffusion from the bulk to the surface layer.

In all the substrate–growing layer systems considered here these processes allow the synthesis to be carried out by a chemical assembly mechanism and the growth of the layer to be controlled very precisely. Allowance is needed for the effect of the concentration and temperature of the reactants, the pH of the solutions and of the wash liquid, the time of treatment and of washing out the reagents, and the method of surface preparation before the synthesis. This is specially true of the synthesis of two or more regions in the layer, including the addition of a doping impurity with a prescribed distribution over the thickness of the layer. All these aspects constitute a fairly complex physico-chemical problem. Therefore at present it is as important to identify the general features of the synthesis in each class of materials (for example, metal sulfides and phosphates) as to produce still more experimental information on the synthesis of the layers, or to systematise it: this approach should allow the prediction and selection of the synthesis conditions for new types of layers. Special attention should be paid to the synthesis by the ionic layer deposition method of layers which cannot be prepared by other methods (for example, owing to the involatility of the starting compounds in the case of synthesis from the gas phase or because of thermal instability).

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