Precursor Design for Chemical Vapour Deposition

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Chemical vapour deposition (CVD) is an attractive method with which to prepare thin films of different materials. There are also steadily increased requirements of new and narrow-property CVD materials. One interesting possibility to meet these requirements is to design the precursor for a special process. Design of precursors for CVD is an emerging field which opens new perspectives for thin-film synthesis. This paper intends to illustrate by a selection of examples how the choice of precursors influences the extension of growth stability regions and how some growth problems may be solved by designing the precursors.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Thin films of different materials today play an important role in fundamental science, as well as in the fields of applied materials and solid-state science. By means of thin-film materials many new phenomena in chemistry, physics, biology and in medicine have been detected and investigated. Microelectronics, sensors, solar cells, metal cutting, corrosion protection and biocompatibility are well-known examples of thin-film applications.

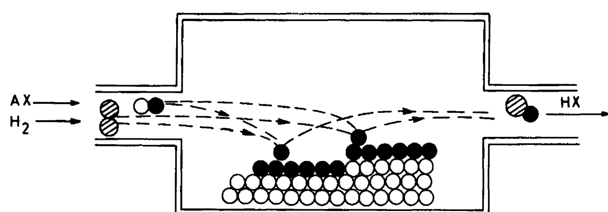


Fig. 1. Principle of chemical vapour deposition.

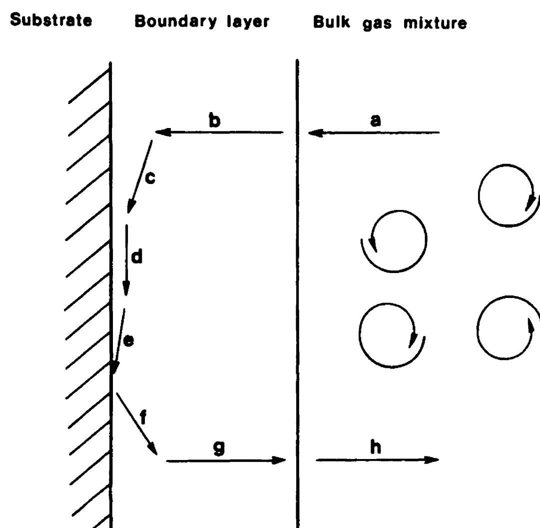


Fig. 2. Process steps in CVD.

With the increased demand for tailor-made, well-defined and high-purity materials the properties of which can be precisely controlled, vapour growth techniques based on chemical reactions have increased in importance. The common name for all these techniques is chemical vapour deposition (CVD), meaning that a solid material is deposited from the vapour through a chemical reaction occurring on or in the vicinity of a substrate surface (Fig. 1). The chemical reactions can be initiated and maintained by heat (thermally activated CVD), photons (e.g. laser-assisted CVD), electrons, ions or in a plasma (plasma-activated CVD).

In a CVD process various sequential steps occur (Fig. 2); transport of reactants to the so-called boundary layer (a), transport across the boundary layer (b), adsorption of the reactants (c), chemical surface reactions (d), nucleation (e, at least at the beginning of the process), desorption of reaction products (f), transport of reaction products across and away from the boundary layer (g and h). From these sequential steps five important reaction zones can be distinguished (Fig. 3): zone 1, homogeneous reactions,

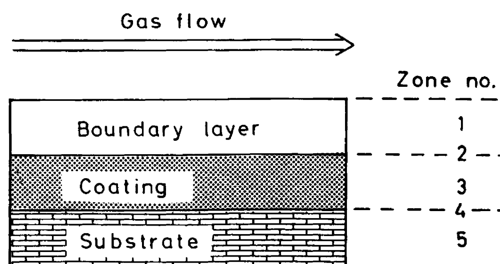


Fig. 3. Reaction zones in CVD.

zone 2, heterogeneous vapour/solid reactions; zones 3–5, solid-state reactions (phase transformation, recrystallization and grain growth). The crystal structure, microstructure, defect content etc. (and hence the properties of the substrate/film composite) are the result of the interplay between reactions taking place in the different zones.

There are two main differences between bulk synthetic and film/surface synthetic (CVD) materials preparation methods:

(i) Part of the growth sequence in film preparation is always adsorption, surface diffusion and incorporation of adsorbed atoms, adatoms, into surface steps. Small amounts of impurities in the system are usually preferentially localized to the surface steps, thus preventing surface diffusing adatoms from being incorporated into the steps. Hence the ideal growth sequence is interrupted, and a new material may be grown. Usually an impurity level of the order of 10 ppm is enough to affect the growth behaviour.

(ii) Only single-phased materials are useful in the application areas for thin films as well as for fundamental research. This means that the reaction pathways have to be controlled in such a way that only one solid reaction product is obtained in, for instance, CVD, while bulk synthetic methods, except for crystal-growth methods, usually give at least traces of other solid phases.

With the increased demand of more sophisticated and also new thin-film materials new requirements are made of the precursors. To control vapour growth processes experimental parameters such as pressure, vapour composition, temperature, gas flows, geometries etc. have been used. For instance, at atmospheric pressure many CVD processes are controlled by the mass transport in the vapour. Going to extremely low pressures such as in an ultra-high vacuum results in growth that is controlled by surface kinetics. In addition to the parameters mentioned above, the design of precursors for the requirements of a specific process opens up new opportunities in the CVD field. This paper discusses, by taking examples from different application areas, what can be achieved by the appropriate selection and design of CVD precursors.

Precursor design for selection and optimization of growth conditions during thermodynamic control

Among the various preparation techniques for high-T_c superconductors, CVD is one of the most versatile, enabling the preparation of massive materials as well as of thin films. CVD allows *in situ* doping during growth and an accurate control of defect content and of oxygen activity in the solid by chemical surface reactions, which affects the critical temperature for superconductivity. Texture, microstructure and density of the deposited material, influencing the current density of the superconductor, are other important areas to be controlled and in which CVD offers unique possibilities. Finally, coatings can be prepared on substrates of complex shape, since all substrate areas exposed to the vapour will be subject to deposition.

CVD of high-T_c superconductors is complicated, since the superconductors are usually composed of at least four elements. A thermochemical analysis of the deposition system usually gives a hint of suitable deposition conditions. The influence of various metal and oxygen precursors on the extension of growth stability regions for $YBa_2Cu_3O_{7-x}$ will be used as an example.

As metal precursors, three groups of compounds can principally be used: organometallic compounds, metal chelates and halides. Organometallic compounds and chelates of the metals Y, Ba and Cu having acceptable vapour pressures exist. However, it is well-known that organometallic and metal chelate precursors in general yield codeposition of carbon, and with oxygen in the vapour, deposition of stable carbonates can be expected. Carbonate deposition may be localized in the grain boundaries of the deposit.

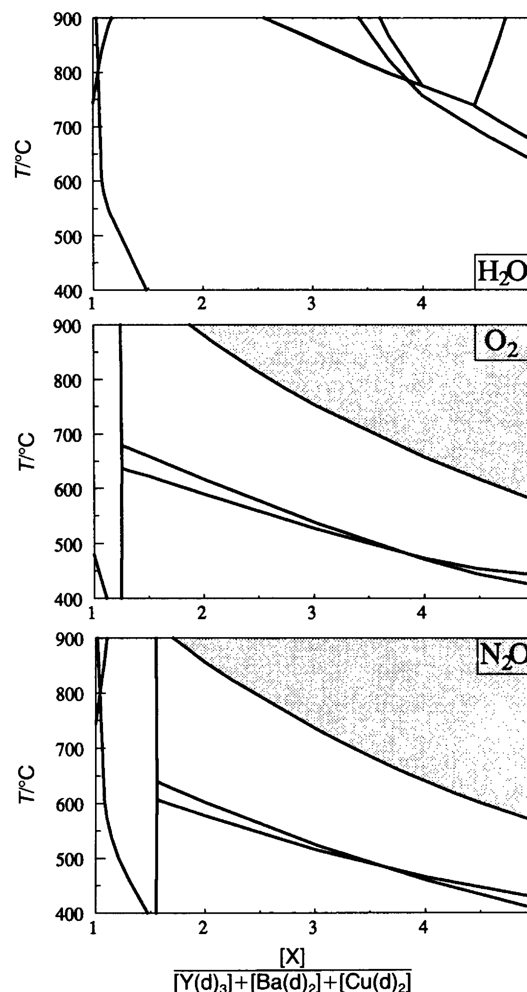


Fig. 4. Calculated CVD diagrams for growth of $YBa_2Cu_3O_{7-x}$ from the dipivaloylmethanates of Y, Ba and Cu (initial molar ratio 1:2:3) and different oxygen sources, total pressure 1 kPa. In the region shaded grey the $YBa_2Cu_3O_{7-x}$ phase is stable.[1]

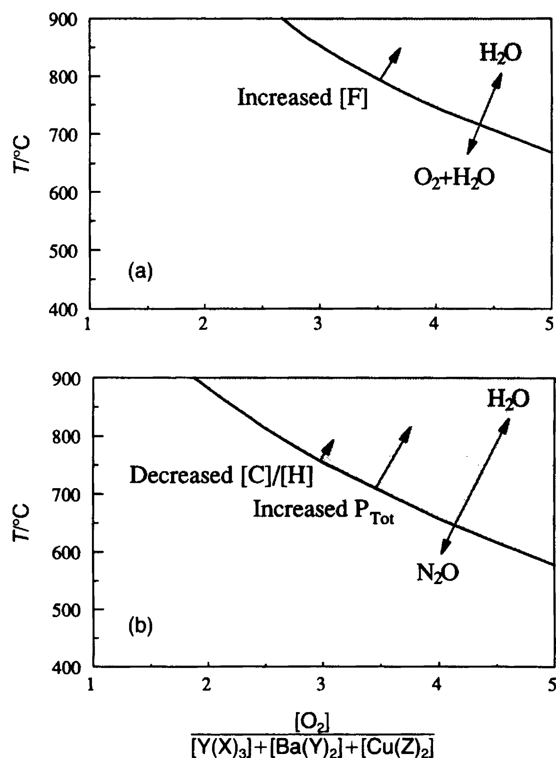


Fig. 5. Trends in the extension of the stability region for $YBa_2Cu_3O_{7-x}$ growth upon changing the oxygen precursors, total pressures or precursor composition for metal chelates (a) with and (b) without fluorine, respectively.[1]

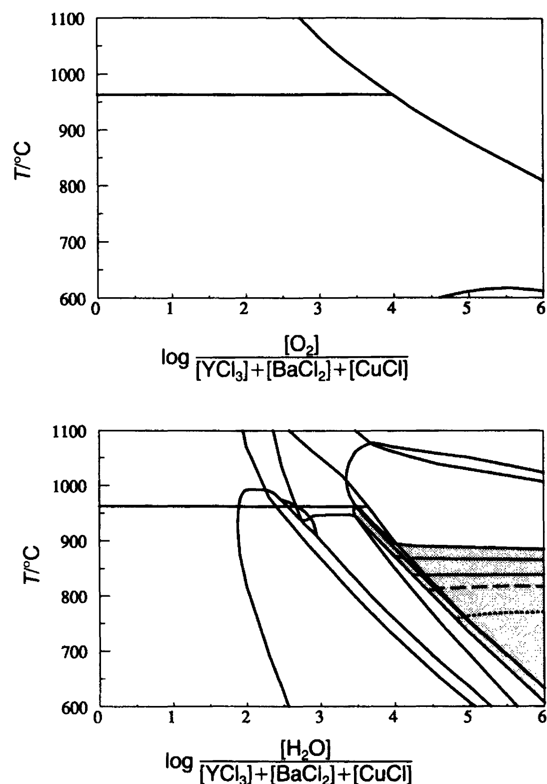


Fig. 6. Stability region for the growth of $YBa_2Cu_3O_{7-x}$ from chlorides of Y, Ba and Cu, respectively (initial molar ratio 1:2:3) from H_2O and O_2, respectively. Total pressure 1 kPa.[3]

This strongly affects the current density even if a very small amount of carbonate is deposited between the grains of a superconductor. For CVD of the $YBa_2C_3O_{7-x}$ phase, different β-diketone metal chelates have been used (e.g. 2,4-pentanedionate or acetylacetonate of copper, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate or simply heptafluorodimethyloctanedionate of barium, 2,2,6,6-tetramethyl-3,5-heptanedionate or dipivaloylmethanate of yttrium), i.e. metal chelates with different metal/carbon/hydrogen/fluorine ratios. The metal halide precursors have considerably lower vapour pressures (solids at room temperature) than the metal chelates (usually liquids at room temperature). The use of metal halides introduces several design problems into the CVD system, but has the advantage of yielding well-defined and clean grain boundaries. Finally, the use of different oxygen sources, O_2, H_2O and N_2O, will be discussed.

Fig. 4 shows calculated CVD diagrams, when dipivaloylmethanates of Y, Ba and Cu are used as precursors together with different oxygen sources. The region in which $YBa_2Cu_3O_{7-x}$, denoted YBCO, is stable is shaded grey. The other phase stability regions are of minor interest in this context and have for simplification not been labelled. As can be seen, N_2O yields the largest deposition area and the lowest deposition temperature. This has been verified experimentally by Tsuruoka *et al.*[2] Without discussing the various metal chelate precursors in detail, their effect on the extension of the YBCO deposition region is qualitatively summarized in Fig. 5. For metal chelates with no fluorine, an increased total pressure, a decreased C/H ratio in the metal chelates or the use of H_2O instead of N_2O shifts the deposition region to higher temperatures. For fluorine-carrying precursors, a decreased fluorine content or the use of a mixture of O_2 and H_2O instead of O_2 moves the deposition region towards lower temperatures.

As mentioned above, metal halides might be quite attractive as precursors for CVD of high-T_c superconductors. Figs. 6 and 7 show the YBCO deposition regions when metal chlorides and metal iodides, respectively, and H_2O and O_2, respectively, are precursors. The YBCO phase can only be deposited with H_2O alone as oxygen source when chlorides are used, mainly because of the stabilities of the metal chlorides and the hydrogen chloride. However, when iodides are used, the opposite situation occurs. The iodides yield a large YBCO deposition region when O_2 is used, whereas it should not be possible to deposit the YBCO phase from the iodides with only H_2O as oxygen source.

The results from the thermochemical analysis, summarized in the various diagrams above, show how the selection of the precursor affects the deposition conditions. For instance, if a low-temperature CVD process is of interest, metal iodides and O_2 should be used as precursors (this has

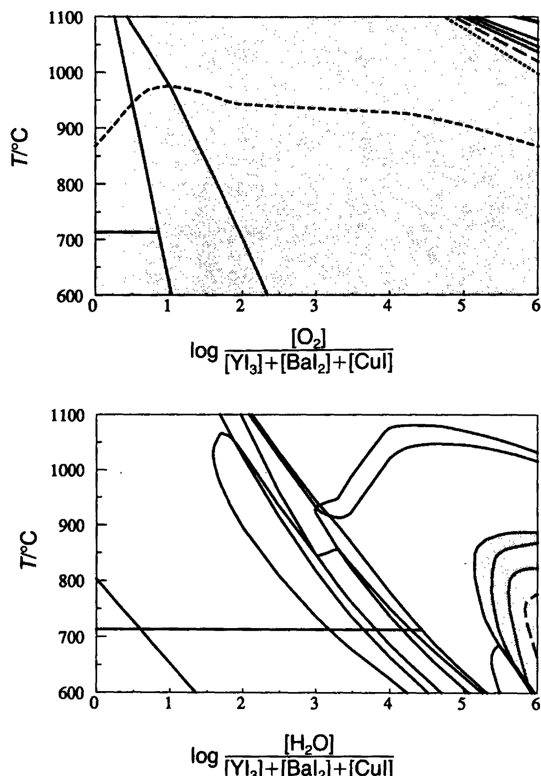


Fig. 7. Stability region of $YBa_2Cu_3O_{7-x}$ from iodides of Y, Ba and Cu, respectively (initial molar ratio 1:2:3) from H_2O and O_2, respectively. Total pressure 1 kPa.[3]

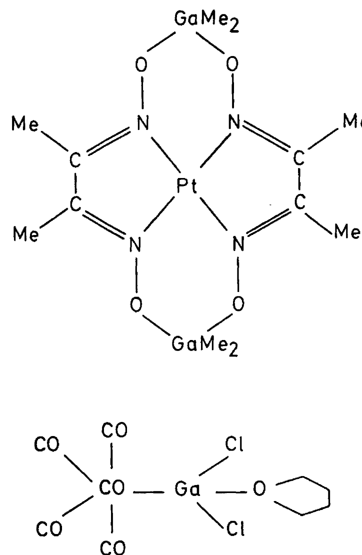
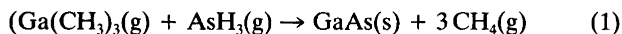


Fig. 8. Structural formulae of dichloro(tetracarbonylcobalt)gallium (III) tetrahydrofuranate and platinum[bis(dimethylglyoximato)bis (dimethylgallium)], respectively.

not been shown experimentally yet). For metal chelates N_2O offers the best conditions for low-temperature deposition.

Precursors for the growth of III–V semiconductors and for the metallization of GaAs

III–V semiconductors are of great interest for the production of high-speed circuits and for optoelectronic and microwave devices. To grow GaAs, trimethyl gallium and arsine are usually used as in reaction (1). However, this



$$(Ga(CH_3)_3(g) + AsH_3(g) \rightarrow GaAs(s) + 3\,CH_4(g) \qquad (1)$$

process has several disadvantages: arsine is very toxic, and trimethyl gallium is pyrophoric. The purity of the precursors and carbon contamination in the grown film are other problems. Finally, for growth of ternary and quaternary compounds, the stoichiometry of the film is hard to control.

Single-source III–V precursors may be one attractive way to solve these problems. Precursors of special interest are those with a strong Ga–As bond and weak bonds to ligands containing carbon and hydrogen. In the selection of precursor those ligands yielding a low carbon contamination in the grown films are the most attractive. Cowley and Jones have reviewed the progress in this field recently.[4]

With a precursor such as $[Me_2GaAstBu_2]_2$, carbon-free GaAs of 1:1 stochiometry could be grown.

For the metallization of III–V semiconductors, thermodynamically stable and lattice-matched metal–semiconductor interfaces have to be designed. Usually pure metals are very reactive towards the semiconductor. The formation of intermediate phases in the interfacial region causes a breakdown in the device junction. Compounds of transition metals and Group III metals are stable towards the semiconductor. For GaAs, the compounds CoGa and $PtGa_2$ are of special interest, since they are not only thermochemically stable in the interfacial region but are also nearly lattice-matched. The stoichiometry of the metallization compound is extremely important for the long-term stability of the device, and a single-source CVD precursor might be useful to control the alloy composition. With dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate and platinum[bis(dimethylglyoximato)bis(dimethylgallium)] (Fig. 8) single-phased films of CoGa and $PtGa_2$, respectively, were grown.[5]

Precursors for area-selective growth

Area-selective growth means that the deposition is localized on desired substrate areas. Principally there exist two possibilities for area-selective growth: the focused beam technique, e.g. by a laser, and the use of patterned substrates.

Pyrolytic laser-assisted CVD. In this method the deposition is localized by pyrolytic decomposition of the molecules adsorbed on and/or colliding with the laser-heated surface.

The reaction spot is defined by the diameter of the focused laser beam, and by both the optical and thermal properties of the substrate and the material deposited. By moving the substrate or the laser beam, materials can be deposited in desired patterns: the technique has also been called direct writing. There are many applications for this technique: e.g. the repair of lithographic masks and of interconnecting conducting circuitry, the growth of monocrystalline filaments perpendicular to the substrate surface, and "personalized" integrated circuits.

Deposition of high-purity metals is an important application area for pyrolytic laser-assisted CVD. However, the requirements of the precursor in this context differ from those in large-area CVD processes. A gaussian temperature profile is obtained around the focused laser spot, which means that the deposition conditions will vary across the spot. For deposition of high-purity metals, precursors yielding only one decomposition product, the metal, over a wide temperature range are needed. This means that stable metal precursors with low-energy decomposition pathways have to be found.

Decomposition of high-purity aluminium at a low temperature is very important in the metallization of integrated circuits. For CVD of aluminium, trimethyl aluminium has been tried. However, carbon-free aluminium can not be grown from this precursor[6] even if the photolytic excimer laser technique and the addition of scavenging gases to the reaction gas are employed.[7] This is basically due to the high stability of $Al(CH_3)$. Baum and Larsson have designed aluminium-carrying precursors with low-energy decomposition pathways.[8] High-purity and carbon-free aluminium lines were deposited with a focused argon-ion laser from trimethylamine hydride. The decomposition of this precursor may probably occur stepwise as shown in reactions (2)–(4). The aluminium hydride is a highly reactive compound and decomposes easily into aluminium and hydrogen. Reactions (2)–(4) probably involve both adsorbed species and vapour species.

$$AlH_3(N(CH_3)_3)_2 \rightarrow AlH_3N(CH_3)_3 + N(CH_3)_3 \qquad (2)$$

$$AlH_3N(CH_3)_3 \rightarrow AlH_3 + N(CH_3)_3 \qquad (3)$$

$$AlH_3 \rightarrow Al(s) + {}^3/_2 H_2(g) \qquad (4)$$

Selective growth on patterned substrates. Localized or so-called selective deposition on desired areas of patterned substrates is an emerging field, with several interesting application areas in microelectronics, sensor and solid-state laser technology, micronics etc. The substrate may be patterned by lithography accompanied by etching. The main steps are shown in Fig. 9. A mask or a passive layer (SiO_2, Si_3N_4, AlN, W, etc.) is grown on the substrate. Openings in the mask are obtained by lithography and etching. Finally, the deposition can be localized on, for instance, the opening in the mask, and an area-selective deposition is then obtained.[9]

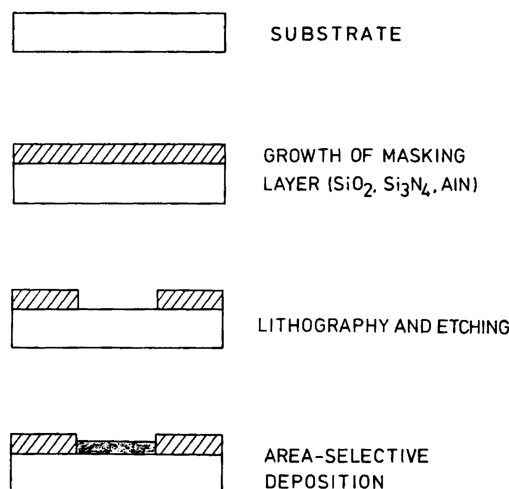


Fig. 9. Opening of a mask in a passivation layer and selective deposition.

For area-selective growth the selectivity is based on differences in the initial interfacial chemical reactions taking place on different substrate materials. The interfacial reactions on one substrate material should be inhibited completely to avoid nucleation, whereas the deposition reactions should be stimulated on those substrate areas where deposition is required. Since the selective deposition in itself is based on differences in chemical interfacial reactions, there are in the processes themselves practically no geometrical restrictions in the dimensions of the deposited areas. Two examples of high-potential area-selective growth systems, illustrating different selective growth principles and where precursor design might be useful, will be discussed below.

Area-selective epitaxial growth of GaAs is of interest for the integration of optonic and electronic devices as well as for solid-state III–V lasers. Epitaxial growth conditions are usually reached at a very low supersaturation or a low driving force for the deposition. For area-selective epitaxy, deposition conditions with an extremely low supersaturation have to be found, so as to avoid nucleation on the mask material. This means that for these conditions the surface concentrations of adsorbed Ga and As on the mask material have to be low. For GaAs epitaxy, $Ga(CH_3)_3$ and AsH_3 are generally used as precursors. However, with these precursors area-selective growth conditions cannot easily be reached and controlled. In particular, the surface concentration of Ga adsorbed on the mask material becomes relatively high. This results in nucleation on the mask material and loss of selectivity. Gallium chlorides are known to be relatively stable. Thus the surface concentration with respect to Ga can be reduced by introducing, for instance, HCl into the system. Kuech and coworkers synthesized an ideal precursor, $Ga(C_2H_5)_2Cl$, for area-selective GaAs epitaxy.[10] With this precursor the surface concentration of Ga on the mask was reduced, mainly by the

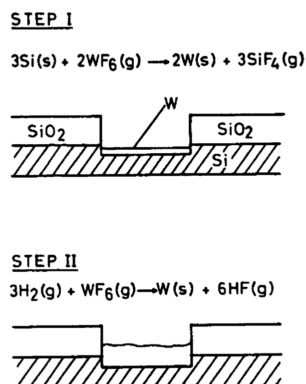


Fig. 10. The two main steps in selective tungsten deposition from WF_6.

formation of GaCl, and nucleation on the mask material could be avoided.

Metallization is a key process step for the realization of the next generation of integrated circuits: tungsten is a promising material because of its resistivity, electromigration resistance and thermal stability. Tungsten can be deposited area-selectively from WF_6 on silicon without any deposition on the adjacent mask.[9] Two main reaction steps can then be distinguished (Fig. 10). In the first step elemental silicon acts as the predominant reducing agent. This results in tungsten deposition on those substrate areas where elemental silicon is exposed to the vapour. The reaction step includes the etching of elemental silicon, i.e. the silicon is consumed. In the second step another reducing agent, H_2, has to take over, since the tungsten film obtained in the first step separates the elemental silicon from the vapour. Because of the fact that the tungsten precursor, WF_6, contains too many fluorine atoms per tungsten atom, the selective tungsten deposition process has several problems, such as encroachment underneath the silicon dioxide, a rough tungsten/silicon interface and tunnel formation into the monocrystalline silicon.[9] On the other hand, fluorine is needed in the precursor in order to localize the deposition onto the areas of elemental silicon. A plausible tungsten precursor, reducing or eliminating the problems mentioned above, may be $W(CO)_xF_{6-x}$. For localization of the deposition, only one fluorine atom per tungsten atom is probably needed. A tungsten precursor such as that suggested above has not been tested yet.

Conclusions

With the increased demand of tailored thin-film materials in science and technology today there is a steadily increasing need for a more precise control of the interfacial chemical reactions that yield film growth. Improved control of interfacial reactions can be achieved in many ways, for instance by precursor design. As discussed above, precursor design may be used to optimize a growth process, control the stoichiometry of the film, reduce the initial substrate etching reactions, avoid secondary nucleation on the mask during selective growth, and to create low-energy decomposition pathways of importance in the pyrolytic laser-assisted metal CVD process. In addition, precursors may be designed for the growth of new materials, low-temperature processing, improved safety and handling, and for long-term stability.

Organometallic precursors have been designed for various processes. In many systems, however, severe contamination of the films by carbon has been observed. Inorganic precursors usually have the advantage of yielding deposits with a low contamination and clean grain boundaries. However, there are a limited number of inorganic precursors with correct compositions and acceptable vapour pressures. Precursor design for CVD processes is one field where a combined effort in synthetic organic and inorganic chemistry might open new perspectives for thin-film synthesis.

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