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A journal devoted to applied physics and chemistry of surfaces and interfaces

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A JOURNAL DEVOTED TO APPLIED PHYSICS AND CHEMISTRY OF SURFACES AND INTERFACES

Editors: D.E. Aspnes, Raleigh, NC, USA J. Nishizawa, Sendai, Japan W.F. van der Weg, Utrecht, The Netherlands

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Advanced ALE processes of amorphous and polycrystalline films

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Abstract

Due to its distinctive self-limiting growth process, Atomic Layer Epitaxy (ALE) technique exhibits a unique combination of advantageous features. In this paper, the benefits and potentials of ALE in growth of amorphous and polycrystalline films will be discussed using some selected processes as examples. These processes include low temperature deposition of high quality nanolaminate dielectrics, controlled deposition of optical multilayers, growth of low resistivity transition metal nitrides using elemental zinc as a reducing agent, and preparation of $ZnS_{1-x}Se_x$ solid solutions via surface anion substitution reactions. The major drawback of ALE, its slowness, and the possibility of overcoming this problem via large-batch processing will also be discussed.

Keywords: Review; Atomic layer epitaxy (ALE); Amorphous thin films; Polycrystalline thin films

1. Introduction

ALE was originally invented for depositing amorphous and polycrystalline films for thin film electroluminescent (TFEL) displays [1] which, in fact, has still remained the most important — if not the only — industrial application of ALE [2,3]. Following the successful introduction of ALE, a great deal of research effort has been devoted to extending its use to other applications as well [2–8]. Though the main interests have concentrated on epitaxial compound semiconductors, substantial progress has also been made with amorphous and polycrystalline films [7– 11].

The advantages of ALE are well known: accurate and simple film thickness control, sharp interfaces, uniformity over large areas, excellent conformality, good reproducibility, multilayer processing capability, and high film qualities at relatively low temperatures. Additionally, from the process design point of view it is important that, unlike in CVD, in ALE solid precursors with relatively low vapor pressures can be used without any difficulty, and that ALE offers a straightforward scale-up to large batches. All these issues together make ALE a potential choice for many applications. In addition, since deposition processes for a wide variety of materials have already been developed (Table 1), a firm basis exists for extending the applied use of ALE. Yet the true application oriented research on amorphous and polycrystalline ALE films has mainly been limited to the TFEL displays [12-19] and solar cells [11,20-27]. On the other hand, besides the conventional thin film applications, ALE has also been examined in preparation of heterogeneous catalysts where the substrates are porous high-surface-area powders [28–30], and recently the excellent conformality achievable in processing of porous substrates was extended to porous silicon [31].

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II–VI compounds	ZnS, ZnSe, ZnTe, ZnS _{1-x} Se _x , CaS, SrS, BaS, CdS, CdTe, MnTe, HgTe, Hg _{1-x} Cd _x Te, Cd _{1-x} Mn _y Te
II-VI based TFEL phosphors	ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb), SrS:M (M = Ce, Pb, Tb)
III-V compounds	GaAs, AlAs, InP, GaP, InAs, $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Ga_xIn_{1-x}P$
Nitrides	
Semiconductors/dielectric	AlN, GaN, InN, SiN _x
Metallic	TiN, TaN, NbN, MoN
Oxides	
Dielectric	Al ₂ O ₃ , TiO ₂ , ZrO ₂ , HfO ₂ , Ta ₂ O ₅ , Nb ₂ O ₅ Y ₂ O ₃ , MgO, CeO ₂ , SiO ₂
Transparent conductors/semiconductors	In ₂ O ₃ , In ₂ O ₃ :Sn, In ₂ O ₃ :F, In ₂ O ₃ :Zr, SnO ₂ , SnO ₂ :Sb, ZnO, ZnO:Al, Ga ₂ O ₃
Superconductors	$YBa_2Cu_3O_{7-x}$
Fluorides	CaF ₂ , SrF ₂ , ZnF ₂
Elements	Si, Ge, Cu
Others	La ₂ S ₃ , PbS, In ₂ S ₃ , CuGaS ₂ , SiC

Table 1				
Thin film	materials	deposited	by	ALE

The major reason for the limited interest to ALE is apparently its slowness. ALE is indeed rather slow when measured in terms of a thickness increment per time unit; with flow-type reactors growth rates of 100–300 nm/h are typically achieved. On the other hand, reasonably high productivities, evaluated in terms of film volume produced per time unit, can be achieved in spite of the low growth rates because of the large-batch/large-area capability. As a convincing example, at maximum as many as 82 glass substrates with dimensions of $155 \times 265 \text{ mm}^2$ are simultaneously processed in the largest ALE reactors in use at Planar International in manufacturing of TFEL displays [32]. This significant difference between the growth rate and productivity should be recognized and carefully considered while evaluating the potentiality of ALE to different applications.

In this paper, the capabilities of ALE to advanced thin film processing will be demonstrated by examining some selected ALE processes on amorphous and polycrystalline films. Special attention will be given to emphasizing the benefits which have been gained by making use of the unique characteristics of ALE.

2. Nanolaminate dielectric films

As a first example of advanced ALE processes, it will be shown how the accurate film thickness control and the multilayer processing capability allow a low temperature deposition of novel dielectrics with high permittivities and low leakage current densities. In addition, due to the excellent large area uniformity of ALE, this approach can easily be scaled up also to large area applications, like the TFEL devices.

High permittivity dielectric films are needed in many devices in micro and optoelectronics. In the TFEL displays, high permittivity insulators should be preferred since they make it possible to use lower driving voltages [19]. Unfortunately, the high permittivity is often accompanied by a high leakage current which prevents the use of these films in their as deposited form. This kind of a problem was met also with the ALE grown Ta_2O_5 films (Fig. 1a) [33].

A common approach to the leakage current reduction has been a use of post-deposition heat treatments, but the required temperatures have usually been too high for the TFEL devices where the glass substrates set an upper limit to the allowed temperature range. Therefore, an alternative strategy relying on multilayer structures has been developed. Originally this strategy was applied for improving the dielectric properties of ALE grown Al₂O₃ films by incorporating thin TiO₂ layers into them [34,35]. Subsequently Kattelus et al. [36] used the same approach with Ta₂O₅ films grown by ALE from TaCl₅ and H₂O. By constructing film stacks of thin Ta₂O₅ and HfO₂ layers, the leakage current density at an electric field of 1 MV/cm could be reduced six orders of magnitude, from 40 mA/cm² for the pure Ta_2O_5 to 40 nA/cm² for the multilayer structure. At



the same time, the HfO_2 incorporation caused only a small decrease of the permittivity from 23–24 for the pure Ta_2O_5 to 20–21 for the multilayer, while values of 13–14 were measured for the pure HfO_2 . The multilayer structures were also found to exhibit reversible breakdown at fields below 5 MV/cm, hence combining this beneficial characteristic of Ta_2O_5 to the low leakage current of HfO_2 .

In the above mentioned study of Kattelus et al., the layer thicknesses within the multilayer structures had to be kept low to have these films applicable to memory circuit capacitors where thin dielectric films are required. By contrast, in the TFEL devices where the insulators are typically about 200 nm thick, more freedom is given to the optimization of the layer thicknesses. Indeed, in our recent study [37] it was shown that the dielectric properties of Ta_2O_5 -HfO₂ nanolaminates can be tailored within a rather broad range simply by varying the layer thicknesses and the relative ratios of the film constituents (Fig. 1). The nanolaminate consisting of 2.5 nm thick layers has its leakage current properties close to those reported by Kattelus et al. [36], but a significant improvement can be gained by increasing the layer thicknesses to about 5 and 15 nm for Ta_2O_5 and HfO₂, respectively (Fig. 1a). As a consequence of the reduced leakage current and only slightly affected permittivity (Fig. 1b), the charge storage factor which serves as a figure of merit for these dielectrics was increased up to 66 nC/mm^2 in the optimized nanolaminates, to be compared with 8

Fig. 1. (a) Leakage current densities of Ta₂O₅-HfO₂ nanolaminates and pure Ta₂O₅ and HfO₂ films as a function of the applied electric field. The films were grown at 325°C using Ta(OC₂H₅)₅, HfCl₄ and H₂O as precursors, and no post-deposition treatments were used. The labels describe the nanolaminate configuration $N \times (d_{\text{Ta}_2\text{O}_5} + d_{\text{HfO}_2})$, where N is the number of Ta_2O_5 -HfO₂ bilayers, and $d_{\text{Ta}_2\text{O}_5}$ and d_{HfO_2} are the thicknesses of single Ta₂O₅ and HfO₂ layers given in nanometers. (b) Permittivities of the Ta₂O₅-HfO₂ nanolaminates versus the relative thicknesses of the HfO₂ layers. (c) Charge storage factors (Q) of the Ta_2O_5 -HfO₂ nanolaminates. Q is defined as $Q = U_{cr}C/S$, where U_{cr} is the critical voltage inducing a leakage current density of 1 μ A/cm², C is the capacitance measured and S is the electrode area. Since Q shows the maximum charge which can be stored at a certain leakage current density, it can be employed in comparing different dielectric films. The labels next to the data points indicate the bilayer thicknesses $d_{\text{Ta}_2\text{O}_5} + d_{\text{HfO}_2}$ [37].

 nC/mm^2 evaluated for both the pure Ta_2O_5 and the pure HfO_2 (Fig. 1c). Rather similar results were obtained also with the Ta_2O_5 – ZrO_2 nanolaminates [38]. It is worth emphasizing that all these nanolaminates were deposited at as low a temperature as $325^{\circ}C$ and no post-deposition heat treatments were used.

It should be noted that in the nanolaminates the leakage current density was lowered also in relation to the HfO_2 (Fig. 1a) or ZrO_2 films. In other words, the addition of layers of the high leakage current material Ta_2O_5 to these films had a positive effect on the leakage current properties. This improvement, which at first sight seems somewhat surprising, is obviously due to the elimination of grain boundaries extending through the whole insulator film from one electrode to another. It is well known that polycrystalline dielectric films, like HfO₂ and ZrO₂ in the present case, exhibit extra conductivity along the grain boundaries. In the nanolaminate structures the continuous grain growth of HfO₂ and ZrO₂, and hence also the continuous grain boundaries, become interrupted by the amorphous Ta₂O₅ layers. Another potential explanation for the improved leakage current properties of the nanolaminates is trapping of electrons at an interface next to a weak point, thereby decreasing the injecting field in the vicinity of this point. However, if these two mechanisms were the only ones responsible for the improvement of the dielectric properties, the layer thicknesses should not have such a significant effect (Fig. 1a). Therefore it appears that also some other, layer thickness dependent factors are involved. Especially the crystalline states of the HfO₂ and ZrO₂ layers, i.e. their crystal structures and crystallite sizes, seem to effect both leakage current and permittivity [37,38].

3. Preparation of optical multilayers

Optical coatings serve as an example of traditional thin film applications where the benefits of ALE make it a potential alternative to the presently used techniques. In optical components dielectric films are widely used, for example in filters and antireflection and high-reflection coatings. The performance of these components is based on interference effects, and the desired spectral responses are realized by constructing stacks of films consisting of materials with different refractive indices. There are several requirements for the films to be used in the optical multilayers: accurately controlled thicknesses, homogeneous and dense bulk like structures, sharp and parallel interfaces, and good thickness and composition uniformities over the whole substrate. Often it is also needed that the multilayer structures are deposited conformally on nonplanar substrates. Naturally, a multilayer processing capability is a prerequisite for an applicable deposition technique. All these requirements are well met by ALE. In fact, these issues are those which are usually considered as the main benefits of ALE over the other techniques. Nevertheless, it was only recently when the use of ALE in preparation of optical dielectric multilayers was demonstrated for the first time [39].

The materials chosen to the first ALE experiments on optical multilayers were ZnS and Al₂O₃ which were grown from the corresponding chlorides and H_2S or H_2O . These processes were developed already during the very first ALE experiments [1], and since that they have reliably served in an industrial production of the TFEL displays for more than a decade. In the optical multilayers ZnS served as a high refractive index material (H) and Al₂O₃ as a low refractive index material (L). The films were so called quarterwave layers, i.e. their optical thicknesses were set to equal one quarter of the wavelength of an interest: $nd = \lambda/4$, where n = refractive index and d = geometrical thickness. The central wavelength λ was arbitrarily chosen to 580 nm. At this wavelength the refractive indices of the film materials were 2.35 for ZnS and 1.68 for Al₂O₃. Thus the desired target thicknesses of the ZnS and Al_2O_3 films were 61.7 and 86.3 nm, respectively.

The simplest two and three layer structures prepared served as antireflection coatings and neutral beam splitters, whereas more complicated multilayer structures were needed in the high-reflection coatings (Fig. 2a) and Fabry–Perot filters (Fig. 2b). The accuracy of the multilayer preparation procedure was checked by comparing the measured transmittance and reflectance spectra with those calculated for the corresponding ideal structures with exactly correct thicknesses and refractive indices. In general a good correspondence was verified. Only in the most complicated structures, i.e. Fabry–Perot filters with a



Fig. 2. (a) Reflectance spectrum of a nine-layer high-reflection coating HLHLHLHLH/glass where H and L refer to quarterwave layers of high and low refractive index materials ZnS and Al_2O_3 , respectively. For comparison a calculated spectrum for an ideal structure with the exactly correct film thicknesses and optical parameters is shown as well. (b) Measured and ideal transmission spectra of a 20 layer Fabry–Perot filter HLHLHLHLHLHLH–LL–HLHLHLHLH/glass [39].

structure of HLHLHLHLH_LL-HLHLHLHLH, rather severe differences were observed in the sideband regions which appear to be very sensitive to even the slightest variations in film parameters (Fig. 2b). Nevertheless, also in this case those spectral regions which are critical for the applications of these devices, i.e. the high peak transmittance at the central wavelength surrounded by a low transmittance region, were well produced in the experimental spectra. It was also verified that the deviations in the side band regions were mainly due to small variations in film thicknesses rather than in refractive indices [39].

These preliminary experiments indicated that ALE is a feasible technique for preparation of optical multilayers. A wide selection of dielectric materials, or more specifically a wide variety of refractive indices, are available by ALE (Table 1) hence allowing a lot of freedom in designing and preparing also much more complicated components than those discussed above. The main problem of ALE arises again from its slowness; the times needed to prepare the 9 and 20 layer structures in Fig. 2 were about 7 and 16 h, respectively. On the other hand, as discussed above the large-batch processing capability offers an effective way for compensating the low growth rate.

4. ALE growth of transition metal nitrides

As compared with CVD, ALE allows more freedom to the choice of precursors because in ALE solids with relatively low vapor pressures can also be used without any difficulty, whereas in CVD their inconstant evaporation rates usually cause problems. An illustrative example of utilizing this advantage is the use of elemental zinc as a reducing agent in ALE growth of transition metal nitride films from the corresponding metal chlorides and ammonia [40,41].

Because the formal oxidation states of the transition metals in their most stable chlorides are usually higher than in their nitrides, a reduction is needed, e.g. $\text{Ti}^{\text{IV}}\text{Cl}_4 \rightarrow \text{Ti}^{\text{III}}\text{N}$. In CVD, this is usually accomplished by a direct action of ammonia or by using hydrogen as an additional reducing agent. These reactions are, however, not very favorable and typically temperatures exceeding 500°C have been needed to achieve materials with low resistivities and acceptable chlorine impurity levels (Fig. 3).

In ALE, the reduction can significantly be enhanced by supplying elemental zinc vapor on the surface between the metal chloride and ammonia pulses. Besides acting as a reducing agent, zinc also removes chlorine from the surface by forming volatile $ZnCl_2$. Thermodynamic calculations have verified that at low temperatures the processes containing zinc are more favorable than those where only metal chlorides and ammonia are involved. In the case of TiN and NbN, for example, the temperature ranges where the zinc containing processes are the most favorable ones extend up to 600 and 950°C, respectively [9,40,41].

Indeed, a comparison between TiN films grown by ALE from $TiCl_4$ and NH_3 with and without zinc revealed significant differences in favor of the zinc containing process [41]. The films deposited at 500°C with zinc had the characteristic golden color of TiN



Fig. 3. A comparison of resistivities (a) and chlorine residue contents (b) of TiN films prepared by ALE from $TiCl_4$, Zn and NH₃ (solid symbols) [41] and by CVD from $TiCl_4$ and NH₃ (open symbols) [42].

and their resistivity was low, about 50 $\mu\Omega$ cm, whereas those grown without zinc were darkish red and had higher resistivities in the order of 250 $\mu\Omega$ cm. As compared with TiN films grown by CVD from TiCl₄ and NH₃, the films prepared by ALE with zinc have substantially lower resistivities (Fig. 3a) which in the first place seems to be due to their low chlorine residue contents (Fig. 3b). In the case of the NbN films, lower resistivities were also obtained with Zn (3 × 10⁻⁴ Ω cm) than without it (6 × 10⁻⁴ Ω cm) [40]. No zinc was detected in any of the TiN or NbN films with Rutherford backscattering spectroscopy (RBS) or energy dispersive X-ray analysis (EDX).

5. Growth of $ZnS_{1-x}Se_x$ films via surface substitution reactions

The stepwise film growth in ALE makes it possible to substitute atoms on the surface of the growing film, thereby offering an alternative approach to a simple and controlled preparation of solid solutions. By combining this strategy with the possibility of using solid precursors, the growth of $ZnS_{1-x}Se_x$ (x = 0-0.8) films from $ZnCl_2$, H_2S and elemental Se has successfully been demonstrated as described in detail elsewhere in this issue by Ihanus et al. [43]. The major benefit of this approach is that the use of the highly toxic H_2Se can be avoided, hence making the process safer and more convenient with no need of extensive safety systems.

The $ZnS_{1-x}Se_x$ films were prepared by using two kind of deposition cycles, one for the pure ZnS (ZnCl₂-H₂S) and one for the incorporation of Se (ZnCl₂-H₂S-Se). The Se content in the films was controlled either by varying the fraction of the Se containing deposition cycles or by adjusting the length of the Se pulse. The highest Se content was achieved by using only the Se containing cycles and increasing the Se pulse length to 3 s, above which the film composition saturated to $ZnS_{0.2}Se_{0.8}$. No film growth occurred if only $ZnCl_2$ and Se were used. This observation verifies that Se was incorporated into the $ZnS_{1-x}Se_x$ films by substituting sulfur atoms on the surface rather than by reacting with the cation containing precursor $ZnCl_2$ [43].

So far this simple preparation of solid solutions via surface anion substitution reactions has been studied only with the $ZnS_{1-x}Se_x$ films. In the near future, the generality of this approach will be examined also with other chalcogenides.

6. Conclusions

In this paper, some advanced ALE processes of amorphous and polycrystalline thin films have been reviewed. A common feature to these processes is that in all of them a simultaneous use of several unique characteristics of ALE has been made. In preparation of both high quality nanolaminate dielectric films and optical multilayers, the simple and accurate film thickness control, multilayer processing capability and excellent large area uniformity give ALE a distinct benefit over the other techniques. The stepwise growth process and the unproblematic use of relatively low vapor pressure solid precursors have been utilized in developing new chemical approaches to transition metal nitride and $ZnS_{1-x}Se_x$ films. Using elemental zinc as an additional reducing agent, the qualities of TiN and NbN films were significantly improved. The incorporation of Se into $ZnS_{1-x}Se_x$ films was, in turn, realized simply by replacing sulfur atoms on the surface of the growing film with elemental Se, thus avoiding the use of the highly toxic H₂Se.

These examples demonstrate how the special characteristics of ALE make it possible both to prepare novel multilayer structures and to utilize unique chemical processes which are not possible in CVD, for example. Obviously ALE offers a great potential for a further development of this kind of unconventional approaches.

In the present paper, it has also been emphasized that the major drawback of ALE, i.e. its slowness, can at least partially be overcome by largearea/large-batch processing. By this way the productivity can be increased to a level where ALE becomes a potential and competitive choice also for industry, as has already been evidenced by its successful utilization in manufacturing of the TFEL displays. Once also this issue becomes generally recognized and considered together with all the other benefits of ALE, it can be expected that the use of ALE will become extended to new areas.

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