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## Metal Fluoride Thin Films Prepared by Atomic Layer Deposition

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#### ABSTRACT

 $CaF_2$ ,  $SrF_2$ , and  $ZnF_2$  thin films have been deposited on glass substrates for the first time using atomic layer deposition (ALD) at temperatures between 260 and 400°C. The source materials used are alkaline earth  $\beta$ -diketonates, zinc acetate dihydrate, and hydrogen fluoride in nitrogen atmosphere. The growth rate of films varies from 20 to 90 pm/cycle depending on materials and temperature. The crystallinity, orientation, stoichiometry, atomic density, optical and electrical properties together with growth properties of the films have been characterized. Also, multilayer structures with alternating materials of high (ZnS) and low (fluoride) index of refraction have been prepared by ALD.

The method of thin film deposition by pulsing two reactants one at a time over substrate surface<sup>1</sup> has been applied to a number of materials.<sup>2</sup> The original name of the method, atomic layer epitaxy or ALE, was applied also to growth on amorphous substrates but here a more specific term atomic layer deposition (ALD) is preferred.<sup>3</sup>

Fluoride thin films have found widespread use in optical coatings<sup>4,5</sup> and as a buffer layer between two crystalline phases.<sup>6,7</sup> The luminescent properties of fluorides have also aroused interest.<sup>8-11</sup> Previously alkaline earth fluorides have been mainly deposited by evaporation<sup>4,5,12</sup> and sputtering<sup>13</sup> although MBE<sup>14</sup> and recently CVD<sup>15</sup> have also been applied. In this paper the growth and properties of SrF<sub>2</sub>, CaF<sub>2</sub>, and ZnF<sub>2</sub> films deposited with ALD technique are investigated.

#### Experimental

The thin film structures were deposited using MC-120 reactor from Microchemistry Ltd., Espoo, Finland, on 5  $\cdot$  5 cm<sup>2</sup> soda-lime glass substrates usually coated with 150 nm thick layer of Al<sub>2</sub>O<sub>3</sub>. The carrier gas was nitrogen from liquid N<sub>2</sub> reservoir and the pressure in the silica reaction chamber was appr. 1 kPa with a gas flow rate 0.3 mmol/s. The basic structure of the reactor is shown in Fig. 1. The system was connected to a rotary vane vacuum pump through chemical and particle filters.

The source materials for cations include zinc, zinc chloride (for ZnS), zinc acetate dihydrate for both fluoride and sulfide<sup>16</sup> and aluminum chloride without additional treatment. Calcium and strontium  $\beta$ -diketonates [Ca(thd)<sub>2</sub> and Sr(thd)<sub>2</sub>, thd = C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>]<sup>17</sup> were synthesized by precipitating metal nitrate by H(thd) in alkaline aqueous solution.<sup>18</sup> All other reagents were commercial. The anion sources were hydrogen sulfide, deionized water and hydrogen fluoride generated by decomposing NH<sub>4</sub>F thermally in the source boat. The hydrogen sulfide gas was administered



Fig. 1. The schematic lay out of the atomic layer deposition equipment.

through a needle valve and the flow was adjusted to  $5 \dots 10$  std. cm<sup>3</sup>/min during continuous flow. The source temperatures are listed in Table I. The rates of evaporation have been calculated using free effusion model,<sup>19</sup> and they represent theoretical upper limits. The desorption is an activated process<sup>20</sup> with an energy barrier at least equal to the heat of adsorption. At low temperatures this is the limiting factor and the free effusion model predicts too high evaporation rates. Above 200°C the potential barrier seems to have a minor effect.

The pulsing sequences used were typically 0.2 s metal precursor pulse followed by 0.5 s nitrogen purge, 0.2 s anion precursor pulse, and 0.7 s nitrogen purge. Multilayer .../ZnS/MF<sub>2</sub>/ZnS/... structures were prepared in the same pumpdown by pulsing reactant materials from separate source boats in different tubes. The nitrogen main flow used was 0.3 mmol/s in CaF<sub>2</sub>, ZnF<sub>2</sub>, and ZnS processes and 0.13 mmol/s in SrF<sub>2</sub> process.

The optical transmission spectra were recorded by Hitachi U-2000 double beam spectrophotometer controlled by a PC computer for determination of film thicknesses, refractive indexes and absorption. Photoluminescent emission and excitation spectra were recorded by Perkin-Elmer LS50 spectrophotometer. Capacitance was measured by HP4192A impedance analyzer.

Table I. Source temperatures and source boat materials. The area of the boat is 3.7 cm<sup>2</sup> and the evaporation rates have been calculated from vapor or dissociation pressure assuming flat surface and free diffusion. For hydrogen sulfide the value is a measured one.

Source material	Temperature (°C)	Boat material	Rate of evaporation (µmol/s)
Al <sub>2</sub> Cl <sub>6</sub>	85	Ti coated with TiO <sub>2</sub>	290
$Ca(thd)_2$	195	Ti coated with TiO <sub>2</sub>	
H <sub>2</sub> S		Pressure cylinder	6
NH₄F	80	Ti coated with TiO <sub>2</sub>	1200
Sr(thd)2	210	Ti coated with TiO <sub>2</sub>	
Zn	280	Borosilicate glass	0.63
Zn acetate	230	Ti coated with TiO <sub>2</sub>	
$\operatorname{ZnCl}_2$	300	Borosilicate glass	1.8

Table II. The growth rates at various deposition temperatures. The films were deposited on an amorphous aluminum oxide layer.

Temperature (°C)	ZnF2 (pm/cycle)	SrF2 (pm/cycle)	CaF <sub>2</sub> (pm/cycle)
260	73		
280	72		
300	77	59	35
320	84	42	$\tilde{24}$
350			25
400			22



Fig. 2. The XRD spectra of fluoride films. The count values have been divided by 20 for  $SrF_2$ (thickness 198 nm, deposited at  $350^{\circ}C$ ) and by 2 for  $ZnF_2$ (310 nm, 300°C) samples. The  $CaF_2$  film is 249 nm thick and deposited at 320°C.

#### **Growth Properties**

The growth temperature of fluoride films has been varied between 260 and 400°C. The growth rates at different deposition temperatures are listed in Table II.

The thermal decomposition of ammonium fluoride produces free ammonia which may participate in reactions with the metal precursors. The final outcome depends on the equilibrium of the following reactions

$$3\text{CaF}_2(s) + 2\text{NH}_3(g) \rightarrow \text{Ca}_3\text{N}_2(s) + 6\text{HF}(g),$$
  
 $\Delta G_{600\text{K}} = +1345 \text{ kJ/mol} [1]$   
 $3\text{ZnF}_2(s) + 2\text{NH}_3(g) \rightarrow \text{Zn}_3\text{N}_2(s) + 6\text{HF}(g),$ 

 $\Delta G_{600K} = +379 \text{ kJ/mol}$  [2]

Ca and Sr behave thermodynamically identically. The reaction enthalpies are so strongly positive that at 320°C the equilibrium is completely on the metal fluoride side. Therefore  $NH_3$  is inert toward the metal fluorides. However, it is quite possible that it reacts with the organic complexes and the reaction products. Most important is that ammonia binds the free hydrogen fluoride before the exhaust gases enter the vacuum pump.

The low growth rate of alkaline earth fluoride films is attributed to the large size of the metal precursor molecules. The cross-sectional area of a M(thd)<sub>2</sub> molecule can be estimated to be 0.56 nm<sup>2</sup> using the length<sup>17</sup> of the thd complex. A full surface coverage then gives metal atom density 1.79 nm<sup>-2</sup>. The cation densities in fluorite crystals CaF<sub>2</sub> and  $SrF_2$  are 24.5 and 20.1 nm<sup>-3</sup>. This translates to theoretical growth rates 73 and 89 pm/cycle, respectively. The observed values on amorphous aluminum oxide surface are 32 and 47% of these maximum growth rates. This can be explained by repulsion of thd-ligands and the limited density of adsorbing anion sites on the surface which lead to a lower attainable surface coverage. Also, the etching effect of free thd-ligands may contribute to the growth rate.<sup>21</sup> The difference of relative growth rates between Ca and Sr fluorides is probably caused by partial decomposition of  $Sr(thd)_2$  in the gas phase.<sup>22</sup> The resulting small size molecules allow higher surface densities of strontium.

Table III. The composition and the atomic density of fluoride films.

Material and growth temperature	Stoichiometry $x_{ m F}/x_{ m metal}$	Atomic density measured	Atomic density bulk values <sup>46</sup>
CaF <sub>2</sub> (320°C)	2.06	$7.1 \cdot 10^{22} \mathrm{~cm^{-3}}$	$7.36 \cdot 10^{22} \text{ cm}^{-3}$
$SrF_2$ (320°C)	2.04	$6.1 \cdot 10^{22} \text{ cm}^{-3}$	$6.10 \cdot 10^{22} \text{ cm}^{-3}$
$ZnF_{2}$ (300°C)	1.99	$9.0 \cdot 10^{22} \mathrm{~cm^{-3}}$	$8.65 \cdot 10^{22} \text{ cm}^{-3}$

In growing  $SrF_2$ , the  $N_2$  carrier gas flow rate was reduced by 60% compared to the flow rate with other fluorides. This reduction in flow improved the thickness uniformity of the  $SrF_2$  film considerably. Because the gas flow is limited by the conductances in the reactor, decreasing the flow rate slowed down the linear velocity of the gas. This apparently gave more time for the thermal decomposition of Sr precursor to attain a final stage so that the species arriving to the substrates had a stabilized distribution of molecular structures.

The relatively high growth rate of  $\text{ZnF}_2$  can be explained analogously with the proposed model for ZnS deposition.<sup>17</sup> The zinc acetate adsorbs as a  $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$  complex. A rough estimate based on bond lengths for its cross section is  $0.71 \text{ nm}^2$ . A full surface coverage gives Zn atom density  $5.62 \text{ nm}^{-2}$  and deposition rate 195 pm/cycle using the cation density 28.8 nm<sup>-3</sup> in the rutile structure. The observed growth rate is 44% of this maximum value. Similar factors as discussed above contribute to this value. The formation of fluoroacetic acid and its etching effect may also affect the low relative growth rate.

Zinc chloride and aluminum chloride did not produce corresponding fluoride films with HF. This fact may be explained by a low sticking coefficient of a metal chloride molecule on a surface covered by fluoride ions. The reason is a strong coulomb repulsion between halide ions. The partial charges<sup>23</sup> of halogen atoms are -0.23 in ZnCl<sub>2</sub> and -0.33 in ZnF<sub>2</sub> calculated with Pauling electronegativities for molecules in gas phase. In ZnS the partial charge of sulfide ion is -0.22 and the electrostatic repulsion energy of Cl<sup>-</sup> ion on ZnS surface can be roughly estimated to be 0.2 eV and on ZnF<sub>2</sub> surface 0.34 eV when the interanion distance is the sum of ionic radii. Assuming other factors to be identical, this repulsion on ZnF<sub>2</sub> surface would reduce the adsorption rate by a factor of 17 compared to ZnS surface at 320°C using an Arrhenius type temperature dependence of kinetics.<sup>24</sup>

With elemental zinc and HF the deposition rate of zinc fluoride film was very low. The same phenomenon has been observed in ALD reactions Zn + S and  $Zn + H_2S$ .<sup>25</sup> This may be attributed to the slow adsorption of atomic zinc. Its ground state  ${}^{1}S_{0}$  with electron configuration  $d^{10}s^{2}$  is quite stable (no unpaired electrons for bonding) and needs 4 eV energy to be promoted to the first excited state  ${}^{3}P$ .<sup>26</sup> Chemisorption of the metal requires oxidation and because univalent Zn is not stable<sup>27</sup> the relatively high ionization enthalpy 27.3 eV for Zn<sup>2+</sup> apparently creates too high a kinetic barrier. Cadmium behaves chemically like Zn but double ionization only requires 25.8 eV and this difference may explain the slightly faster atomic layer deposition rate of CdS <sup>28</sup> and CdTe <sup>29</sup> using elemental cadmium.



Fig. 3. The indexes of refraction of fluoride films. The values are calculated by fitting a one term Sellmeier model to the measured transmission spectra. The literary values for bulk materials at wavelength 589 nm are 1.4338 for CaF<sub>2</sub>,<sup>38</sup> 1.442 for SrF<sub>2</sub>,<sup>46</sup> and 1.502 for ZnF<sub>2</sub>.<sup>47</sup>



Fig. 4. Optical absorption in  $ZnF_2$  and  $SrF_2$  films. The measured transmission has been divided by transmission calculated for a nonabsorbing film. The samples from the top are: 247 nm  $SrF_2$  (deposited at  $320^{\circ}$ C), 347 nm  $ZnF_2$  ( $300^{\circ}$ C), and 426 nm  $ZnF_2$  ( $300^{\circ}$ C), acceasing the deposition temperature below  $300^{\circ}$ C does not further reduce the absorption in the zinc fluoride.

#### **Film Properties**

X-ray diffraction spectra of the fluoride films are shown in Fig. 2. The crystallinity of the  $SrF_2$  film is similar to that of zinc sulfide deposited by  $ALD^1$  whereas zinc and calcium fluoride are much poorer in this respect.

The main reflection in the  $\text{ZnF}_2$  sample is [011]. In rutile structure this surface contains only one type of atom. Therefore it seems that the growing crystal facet tends to form complete layers of ions. The main diffraction peak of  $\text{SrF}_2$  is [111] on which surface both ions are exposed in fluorite structure. This same orientation has been observed to dominate also in evaporated films on glass.<sup>30</sup> In alkaline

Table IV. Electrical properties of the fluoride films at room temperature. The low field resistivity is the value linearly extrapolated to zero field.

Material	$\begin{array}{c} \text{Permittivity} \\ \text{measured} \\ (\epsilon_0) \end{array}$	$\begin{array}{c} \text{Permittivity} \\ \text{bulk value} \\ (\epsilon_0) \end{array}$	F <sub>0</sub> (kV/cm)	$J_0$ (pA/cm <sup>2</sup> )	Low field resistivity $(T \ \Omega-cm)$
$CaF_2$ SrF <sub>2</sub> ZnF <sub>2</sub>	$7.0 \\ 6.7 \\ 7.4$	${\begin{array}{c} 6.76^{32} \\ 7.69^{48} \end{array}}$	1.3 0.89 18.6	$2.9 \\ 0.05 \\ 0.76$	$110 \\ 170 \\ 17,500$

earth fluorides the surface energy density of this interface is particularly  $low^{31}$  and it is the natural cleavage plane. In CaF<sub>2</sub> the [220] peak is also strong while in SrF<sub>2</sub> it is barely visible. Evaporated CaF<sub>2</sub> has been reported to have a random orientation on silicon oxide at high temperatures.<sup>32</sup>

The areal density of atoms and the film composition were determined using Rutherford backscattering spectroscopy<sup>33</sup> with <sup>4</sup>He ion beam and the thickness was obtained by optical measurement. The results have been collected in Table III. It seems that the alkaline earth fluoride films contain a small excess of anions while  $\text{ZnF}_2$  is stoichiometric within the measurement resolution. The packing density in  $\text{CaF}_2$  is practically the same as reported for a film<sup>34</sup> evaporated at 300°C.

The carbon contamination was analyzed by ion backscattering spectroscopy using a  $^{12}C(\alpha,\alpha)^{12}C$  resonance reaction at <sup>4</sup>He ion beam energy 4265 keV. The carbon concentration level is about 0.5 atom-% in films deposited using either  $\beta$ -diketonate or acetate precursor.

The fluoride precursor reacts with soda-lime glass surface above  $300^{\circ}$ C (no attack on silica was observed), and fluoride films were therefore deposited on amorphous aluminum oxide or polycrystalline ZnS films. A thin layer (*ca.* 10 nm) of Al<sub>2</sub>O<sub>3</sub> is converted to AlF<sub>3</sub> which has a low vapor



Fig. 5. The electroluminescent and photoluminescent spectra of a 120 nm thick CaF<sub>2</sub>:Eu film. The film was deposited at 400°C. Bottom dielectric is titanium-aluminum oxide and the top dielectric is sputtered AIN.

Fig. 6. The current density as a function of electric field. In this log (current) vs. square root of field presentation the plots are almost linear. The film thicknesses are  $SrF_2$  295 nm,  $ZnF_2$  354 nm, and  $CaF_2$  249 nm.

pressure and thereafter passivates the surface while ZnS is thermodynamically stable. The thicknesses and optical properties of the films were determined by fitting the measured transmission spectrum to a theoretically computed one.<sup>35</sup> The estimated inaccuracy of the fluoride film thickness on Al<sub>2</sub>O<sub>3</sub> layers is  $\pm 10$  nm.

The refractive indexes of the fluoride films were modeled by one oscillator which gives the one term Sellmeier model $^{36}$ 

$$n^{2} = 1 + \frac{A}{1 - (\lambda_{r}/\lambda)^{2}}$$
[3]

where A is the oscillator strength and  $\lambda_r$  its resonant wavelength. For  $\text{ZnF}_2$ ,  $\lambda_r$  is 150 nm but for other fluorides it is below the range of determination. The indexes of refraction have been plotted in Fig. 3 as a function of wavelength.

In the zinc fluoride film there exists losses well above the fundamental absorption edge 160 nm<sup>11</sup> of pure  $\text{ZnF}_2$ . The measured transmission divided by the calculated absorption free transmission has been plotted in Fig. 4. The absorption increases with deposition temperature above 300°C and is obviously related to thermal decomposition of zinc acetate because at 400°C the zinc acetate gives a black residue on the walls of the source tube.

Photoluminescent emission is a wide band centered at 500 nm in all fluorides and excitation efficiency increases

monotonically with quantum energy below 250 nm wavelengths. The bandgap (CaF<sub>2</sub> 12.2 eV,  $^{37}$  ZnF<sub>2</sub> about 7 eV)^{11} is above the available excitation energy 6.2 eV and the observed fluorescence is apparently due to some defect states in the films as is often the case with fluorides.  $^{38}$ 

The primary interest for preparing these fluoride films was to investigate their electroluminescent properties.<sup>39</sup> The standard alternating current thin film EL device (ACTFEL) consists of a phosphor layer between two dielectric layers<sup>40</sup> with metal and transparent indium-tin oxide (ITO) electrodes. In this structure CaF<sub>2</sub> film doped with europium exhibits violet ac electroluminescence (Fig. 5). The light emitting transition is from the lowest state of the 4f<sup>6</sup> (<sup>7</sup>F) manifold to the ground state <sup>8</sup>S. <sup>37</sup> The CIE-color coordinates of the hue are x = 0.20, y = 0.10. The dominating wavelength of CaF<sub>2</sub>:Eu is 450 nm which is shorter than the value 464 nm in the standard CRT blue phosphor. This is the wavelength of monochromatic radiation which, when mixed with white (e.g., CIE-E) light, produces the same color as the observed emission spectrum. The saturation luminance with 1 kHz sinusoidal drive was 2 cd/m<sup>2</sup> which is almost the same as reported for the bluish white emission from ZnF<sub>2</sub>:Tm.<sup>41</sup> This value is almost two decades below the required level for display applications. Red emission at 680 nm from interstitial divalent europium<sup>42</sup> has not been observed.







Fig. 8. Optical transmission spectrum of a sample with 21 layers of ZnS and SrF<sub>2</sub>. The circles are measured points and the curve is calculated. Average error in the fitting is 2%. The top ZnS is 89 nm, SrF<sub>2</sub> 20 nm, intermediate ZnS 60 nm and bottom ZnS 100 nm. The total thickness of the film stack is 930 nm.

Electrical characteristics were measured by depositing the fluoride films on substrates coated with  $Al_2O_3$  and ITO patterned to row lines. Aluminum was then sputtered on the top and formed to isolated capacitors with an area of 36 mm<sup>2</sup>. Capacitance was measured at 10 kHz and 1 V and relative permittivities in Table IV were calculated using film thicknesses determined from the film deposited on  $Al_2O_3$  at the same growth run. Optical absorption in the ITO layer makes it unsuitable for thickness determination. The accuracy of the permittivity due to film thickness uncertainty is about  $\pm 20\%$ .

Table V. Structure parameters of a sample with 21 layers deposited in one pump down. The sample was prepared at 320°C using Zn acetate, H<sub>2</sub>S, Sr(thd)<sub>2</sub> and NH<sub>4</sub>F. In the determination of the film thicknesses all the strontium fluoride layers were assumed to be identical as well as the thin ZnS films. *n* is the index of refraction.

Repetition	Layer	Cycles	Thickness	<i>n</i> at 580 nm
1 9 1 1	$ZnS SrF_2/ZnS SrF_2 ZnS Substrate$	300 100/200 100 300	55 nm 8.2/37 nm 8.2 nm 52 nm 1.1 mm	$2.33 \\ 1.44/2.33 \\ 1.44 \\ 2.33 \\ 1.53$

The current *vs.* electric field curves in Fig. 6 were fitted by a model applicable to both Schottky or Poole-Frenkel type conduction<sup>43,44</sup> at sufficiently high fields

$$J = J_0 e^{\sqrt{F/F_0}} \tag{4}$$

where *J* is the current density and *F* is the electric field. The material parameters  $J_0$  and  $F_0$  have been listed in Table IV. The relatively low resistivity and breakdown field are similar to those reported for calcium fluoride films deposited with MBE on Si <sup>45</sup> whereas in sputtered films a resistivity as low as 10<sup>9</sup>  $\Omega$ -cm has been observed.<sup>13</sup>

The electrical characteristics of an ACTFEL device are studied by plotting the integrated current as a function of applied voltage.<sup>40</sup> These charge-voltage loops are shown in Fig. 7 with different peak driving voltages. The steady widening of the loop with voltage indicates that the conductivity increases gradually with electric field. This is in distinct contrast with conventional ZnS and SrS devices which exhibit a sharp breakdown at a well-defined threshold point.

The optical transmission spectrum of a  $ZnS/SrF_2$  multilayer structure in Fig. 8 exhibits the steepness of the pass bandedge achievable in an interference filter. The measured transmission at 370 nm is less than 0.5%. The thicknesses of the layers are obtained by fitting the measured



Fig. 9. Measured and calculated RBS spectra of a multilayer sample in Table V. Layer numbers are in parenthesis and numbering begins from the topmost layer. The layer thicknesses from the optical modeling are used except that the layers 7-20 have been replaced with one layer with an average composition. The first two films containing Sr (2, 4) and the first Zn layer (1) are clearly resolved. Also the first three sulfur containing layers (1, 2, 3) are visible.

transmission data to a theoretically calculated spectrum.<sup>35</sup> A good fit is achieved by using materials with zero extinction coefficients. An RBS spectrum of a sample with parameters in Table V is shown in Fig. 9. The first sulfide and fluoride layers are clearly resolved. This shows that ALD is well suited for preparing multilayer stacks for optical filter applications.

#### Conclusions

The growth of MF<sub>2</sub> films by atomic layer deposition has been demonstrated for the first time. The growth properties are good although the deposition rate of  $CaF_2$  is somewhat low. The films are polycrystalline and the density is close to the bulk values. Alkaline earth fluoride films have low optical absorption, but ZnF<sub>2</sub> exhibits impurity related losses at the short wavelength end of the visible spectrum. Because of the compatibility with the ZnS deposition with ALD these materials are suitable for multilayer antireflection coatings and optical filters. Electrically these fluoride films are poor insulators and, when doped with rare earths, they give low electroluminescent emission intensity.

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### Oxygen Incorporation during Low Temperature Chemical Vapor Deposition Growth of Epitaxial Silicon Films

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#### ABSTRACT

We have studied the incorporation kinetics of oxygen during the chemical vapor deposition (CVD) growth of epitaxial silicon and silicon-germanium layers at temperatures between 700 and 750°C. In this temperature range, the incorporation of oxygen into the growing film is a kinetically driven process and is not governed by equilibrium conditions. Oxygen concentrations exceeding the solid solubility for interstitial oxygen in silicon can be incorporated into the epitaxial layers. We determine an effective sticking probability for oxygen on the surface of silicon under CVD growth conditions and find it to be 100 times lower than that found in ultrahigh vacuum experiments. This reduction in sticking is due to both hydrogen surface coverage and boundary layer effects. We also have determined the maximum oxygen contamination level allowed in the gas stream for the CVD growth of low oxygen content silicon films.

The role of oxygen in the silicon has been studied extensively since the beginning of the semiconductor era. Characteristics of oxygen in bulk silicon emerged in the middle 1950s with the infrared absorption work of Kaiser et al.<sup>1,2</sup> Many properties of oxygen in Czochralski grown silicon were found to be beneficial, such as the added mechanical strength<sup>3</sup> and metallic gettering properties<sup>4,5</sup> due to oxygen precipitates. The interaction of oxygen with the silicon surface also has received endless attention because of the importance of SiO<sub>2</sub> to the electronics industry (Ref. 6 contains an extensive reference list of work in this area). Surface scientists have concentrated on the initial formation of chemical bonds and the stability of oxygen on silicon surfaces over a wide range of temperatures.<sup>7,8</sup>

Here, we investigate the surface interaction of oxygen and silicon during low temperature CVD by studying the incorporation of oxygen during the growth of epitaxial silicon layers. This study is to determine the conditions for the growth of high quality silicon (and silicon-germanium) epitaxial layers by CVD performed at temperatures <800°C. To determine conditions for the growth of high quality films, we must study the characteristics of oxygen incorporation during CVD. With this information we can determine the effective sticking coefficient for oxygen under growth conditions and proceed to determine the conditions for growing low oxygen content films.

#### Background

For any crystalline growth technique, a clean defect-free surface is needed for epitaxial growth. During silicon epi-

taxy, surface oxide formation can break the pattern of the silicon surface and cause noncrystalline growth and highly defective films through the formation of stacking faults and hillock structures.<sup>9,10</sup> Experimental results of oxygen stability on the silicon surface have been used as guidelines by which operating points for epitaxial reactors are designed. Figure 1 describes the stability of oxygen on clean (100) silicon in 600 to 1000°C and is from the experiments of Lander et al.<sup>8</sup> The work demonstrates the competing processes of adsorption of oxygen to form  $SiO_2$  and desorption of oxygen as SiO with the following reactions

$$\frac{1}{2}O_2 \rightarrow O(ads)$$
 [1]

$$Si + 2 O(ads) \rightarrow SiO_2$$
 [2]

$$Si + SiO_2 \rightarrow 2SiO(g)$$
 [3]

where Eq. 1 and 2 describe the adsorption of oxygen and the formation of SiO<sub>2</sub>, and Eq. 3 describes the desorption of oxygen in the form of SiO. Similar experiments were per-formed by Ghidini *et al.*<sup>7,11</sup> to extend the results to higher substrate temperatures and oxygen pressures.

According to the Lander study, as the partial pressure of oxygen in the chamber increases and the substrate temperature decreases, oxygen remains more stable on the silicon surface. The result is the formation of SiO<sub>2</sub>. The sticking probability of oxygen on the clean silicon surface (no passivating layer) has been determined as approximately 0.01  $^{12}$ and relatively independent of temperature. Under the conditions of high substrate temperature and low oxygen pressures, the surface remains free of oxygen due to the desorp-

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