Effect of Al Distribution on Carrier Generation of Atomic Layer Deposited Al-Doped ZnO Films

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The effect of the Al distribution on the electrical properties of Al-doped ZnO (AZO) films deposited by atomic layer deposition (ALD) is investigated. In order to control the Al distribution, the pulsing time of trimethylaluminum (TMA) is varied from 2 (within an ALD window) to 0.1 s. As a result, the areal density of Al atoms incorporated in a single dopant layer decreases from $3.3 \times 10^{14}$ to $1.2 \times 10^{13}$ cm$^{-2}$. Hall measurements reveal that the minimum resistivity of the ALD-AZO films is decreased from $3.2 \times 10^{-3}$ to $1.7 \times 10^{-3}$ Ω cm as a result of reducing the TMA pulsing time from 2 to 0.1 s. This decrease is due to the obvious increase of the carrier concentration from $1.4 \times 10^{20}$ to $4.7 \times 10^{20}$ cm$^{-3}$. It is suggested that both the improved doping efficiency (from 13 to 58%) and the insertion of more dopant layers within the ZnO matrix are responsible for the increase of the carrier concentration.

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Experimental

AZO films were deposited on SiO$_2$ (100 nm)/Si substrates using a showerhead-type GENI-MP1000 ALD system (ASM-Genitech, Inc.) at a deposition temperature of 200°C and a working pressure of 3 Torr. Diethylzinc (DEZ) and trimethylaluminum (TMA) were used as precursors for the deposition of ZnO and Al$_2$O$_3$ and water vapor was used as a reactant. For the delivery of DEZ and TMA molecules into a chamber, Ar was used as a carrier gas with a flow rate of 5 s ccm (standard cubic centimeter per minute). Pulsing times of DEZ and water vapor were fixed to 2 s, while the pulsing time of TMA was varied from 0.1 to 3 s. For instance, the Langmuir exposure of the TMA was ~0.1 Torr s for 2 s pulsing and ~0.005 Torr s for 0.1 s pulsing, respectively. The Ar purge gas was flown for 5 s beginning right after the injection of the precursor and the water vapor. The doping concentration of the AZO films were varied by repeating various numbers of ZnO ALD cycles ($R_{ALD}$) and 1 ALD cycle of Al$_2$O$_3$ for a total of 200 ALD cycles. Film thickness was measured using an ellipsometer ($\lambda$: 632.8 nm). Film composition was analyzed by Auger electron spectroscopy (AES, Perkin-Elmer/PHI 660). Resistivity, Hall mobility, and carrier concentration were measured using a Hall measurement system (BIO-RAD, HL5500PC).

Results

Control of the amount of Al atoms in a single dopant layer.—As suggested above, it is necessary to reduce the areal density of Al atoms in a single dopant layer in order to improve the doping efficiency of the ALD-AZO films. This can be achieved by reducing the surface coverage of the precursor. From the Langmuir isotherm, the surface coverage of the precursor is dependent on both the reaction time and partial pressure. Therefore, in this study, we varied the pulsing time of the TMA molecules ($t_{TMA}$) to control the areal
density of Al atoms incorporated during one ALD cycle. Figure 1 shows the film growth rate of ALD-Al$_2$O$_3$ deposited on Si substrates as a function of $t_{\text{TMA}}$. The films exhibited a growth rate of almost a constant value between 0.13–0.14 nm/cycle when $t_{\text{TMA}}$ was longer than 1 s (ALD processing window). Meanwhile, the film growth rate decreased below 0.13 nm/cycle if $t_{\text{TMA}}$ was shorter than 1 s due to the limited reaction time. As shown in the plot, the growth rate decreased to 0.116 nm/cycle at a $t_{\text{TMA}}$ of 0.1 s.

Based on the results in Fig. 1, $t_{\text{TMA}}$ was varied among the values of 2 (surface-saturated condition), 0.5, and 0.1 s (reduced conditions) for the deposition of ALD-AZO films. Figure 2a shows the relative intensities of the Al AES signal [=$I_{\text{Al}}/(I_{\text{Zn}} + I_{\text{Al}})$] where $I_{\text{Zn}}$ and $I_{\text{Al}}$ are the intensities of the Zn and Al AES signals, respectively] through a film growth direction. These films were deposited with an ALD cycle ratio of ZnO:49:Al$_2$O$_3$ 1. As is shown in Fig. 2a, all Al signals exhibited 4 peaks (including one at the top) showing that these films have distinct layered structures. It is also noted that the relative intensities were obviously lowered when reducing $t_{\text{TMA}}$ from 2 to 0.1 s. Based on the average intensities, the areal density of Al atoms incorporated in a single dopant layer ($N_{\text{Al}}$) was estimated in Fig. 2b. From the density of the ALD-Al$_2$O$_3$ film (2.91 g cm$^{-3}$) and the incubation time on the ZnO surface ($\sim$70%), we determined $N_{\text{Al}}$ to be $\sim$3.3 $\times$ 10$^{13}$ cm$^{-2}$ when the surface-saturated condition is used ($t_{\text{TMA}}$: 2 s). Under the reduced conditions ($t_{\text{TMA}}$: 0.5 and 0.1 s), $N_{\text{Al}}$ values were estimated by comparing the average intensities of their respective AES signals. As shown in Fig. 2b, $N_{\text{Al}}$ clearly decreased to $\sim$1.2 $\times$ 10$^{13}$ cm$^{-2}$ by reducing $t_{\text{TMA}}$ to 0.1 s. This decrease is more evident than the decrease on the ALD-Al$_2$O$_3$ surface (Fig. 1) probably due to the different growing surfaces. These results represent the controllability of the amount of Al atoms in a single dopant layer by controlling the deposition conditions.

Effect of Al distribution on electrical properties of ALD-AZO films.—The electrical properties of ALD-AZO films with different $N_{\text{Al}}$ values were investigated by Hall measurement. Figure 3 shows the resistivity of ALD-AZO films deposited with various $t_{\text{TMA}}$ values of 2, 0.5, and 0.1 s. In Fig. 3a, the x-axis indicates an ALD cycle ratio of Al$_2$O$_3$ compared to the total number of ALD cycles. The resistivity initially decreased as the Al$_2$O$_3$ cycle ratio increased and then it increased after a certain cycle ratio regardless of the $t_{\text{TMA}}$ value. Meanwhile, the Al$_2$O$_3$ cycle ratio of the films that exhibited the lowest resistivities (indicated by arrows) increased as the $t_{\text{TMA}}$ value decreased. This indicates that more dopant layers are inserted to reach the minimum resistivity if $N_{\text{Al}}$ is reduced (Table I). Figure 3b shows the resistivity as a function of the atomic ratio of Al compared to the total cations [Al/(Al + Zn)]. Herein, the Al atomic ratio was assumed to be as follows

$$\frac{[\text{Al}]}{[\text{Al}+\text{Zn}]} = \frac{N_{\text{Al}}}{N_{\text{Al}} + 0.81 \times 4 \times N_{\text{Zn}} + (R_{\text{ALD}} - 4) \times N_{\text{Zn}}}$$

where $N_{\text{Zn}}$ is the number of Zn atoms deposited for one ALD cycle ($\sim$9.4 $\times$ 10$^{14}$ cm$^{-2}$) and $R_{\text{ALD}}$ is the ALD cycle ratio of ZnO to Al$_2$O$_3$. In this equation, the incubation time of ALD-ZnO on the Al$_2$O$_3$ was considered. For instance, in the previous in-situ quartz crystal microbalance study of ALD-AZO, it was reported that only $\sim$81% of the Zn atoms were deposited during the initial four ALD cycles right after the Al$_2$O$_3$ cycle. After those cycles, the amount of Zn deposited every cycle was considered to be constant as $N_{\text{Zn}}$. As shown in Fig. 3b, for a similar doping concentration, the AZO films deposited with the reduced $t_{\text{TMA}}$ exhibited relatively lower resistivities compared to the surface-saturated condition ($t_{\text{TMA}}$: 2 s). For instance, the minimum film resistivity decreased from 3.2 $\times$ 10$^{-3}$ to 1.7 $\times$ 10$^{-3}$ $\Omega$ cm as $t_{\text{TMA}}$ was reduced from 2 to 0.1 s.

Figure 1. Film growth rate of ALD-Al$_2$O$_3$ as a function of TMA pulsing time. The film growth rate was calculated by dividing the film thickness by the number of ALD cycles. Arrowed region indicates an ALD window which exhibits a constant film growth rate.

Figure 2. (Color online) (a) Relative intensities of the Al AES signals in ALD-AZO films deposited with various TMA pulsing times. The ALD cycle ratio of these films is ZnO 49:Al$_2$O$_3$ 1. Sputtering time of each film is rescaled to show similar peak positions. (b) The areal density of Al atoms incorporated in a single dopant layer ($N_{\text{Al}}$) as a function of TMA pulsing time.
This result indicates that the electrical properties of ALD-AZO films are strongly dependent on the areal density of Al atoms in a single dopant layer.

Figures 4a and 4b show the Hall mobilities and carrier concentrations of the ALD-AZO films, respectively. These plots are also converted with respect to the Al atomic ratio. In Fig. 4a, the Hall mobility decreased as the Al atomic ratio increased for all cases. Interestingly, the films deposited with the reduced \( t_{TMA} \) values (0.5 and 0.1 s) exhibited relatively lower Hall mobilities as shown in Fig. 4a and Table I. This is probably due to the higher carrier concentration in the case of the reduced \( t_{TMA} \), which can result in the increase of ionized impurity scattering.\(^{27,28}\) In contrast, in Fig. 4b, the carrier concentration increased remarkably when reducing \( t_{TMA} \). The maximum carrier concentration at a \( t_{TMA} \) of 0.1 s was as high as \( \sim 4.7 \times 10^{20} \) cm\(^{-3} \), which is approximately three times higher compared to the film obtained at the saturated condition (\( t_{TMA} \): 2 s). This value is even comparable to that of the ALD-ITO films.\(^{8,29}\) Therefore, it is clear that the decrease of the resistivity with shortening \( t_{TMA} \) is due to the increase of the carrier concentration.

In Fig. 4b, it should be noted that the carrier concentration increased greatly when reducing \( t_{TMA} \) value. That is, the carrier generation behavior was enhanced by reducing \( N_{Al} \). The doping efficiency \((\eta)\) can be simply defined as

\[
\eta = \frac{\Delta n}{c_{Al}} = \frac{n_{AZO} - n_{ZnO}}{c_{Al}}
\]

where \( \Delta n \) is the increase of carrier concentration due to the doping, \( n_{AZO} \) and \( n_{ZnO} \) are the carrier concentrations of AZO films and the undoped ZnO film (\( \sim 3.3 \times 10^{19} \) cm\(^{-3} \)), respectively, and \( c_{Al} \) is the actual doping concentration. As summarized in Table I, the doping efficiency was improved from 13 to 58% by reducing \( t_{TMA} \) from 2 to 0.1 s. It is conceivable that the decrease of \( N_{Al} \) would be responsible for this improvement. As \( N_{Al} \) decreases from \( 3.3 \times 10^{14} \) to \( 1.2 \times 10^{14} \) cm\(^{-2} \), the average spacing between Al atoms increases from 3.5 to 9.1 Å. This would bring about more oxygen-deficient...
AlO₆ by making the formation of Al-O-Al bondings less probable. Because oxygen-deficient AlO₆ can take oxygen from the ZnO matrix and provide doubly-charged donors (V⁺⁺/Zn⁺⁺), the decrease of \( N_{Al} \) would result in the improved doping efficiency as presented in this study.6,17

Figure 5. (Color online) (a) increase of carrier concentration due to doping \((\Delta n)\) with respect to the density of dopant layers \((m_{AlO})\). Arrows indicate the maximum \(\Delta n\). (b)–(c) Schematic distribution of Al atoms (red dots) in the films deposited with the (b) surface-saturated condition and (c) reduced TMA pulsing time.

**Discussion**

Recently, we reported that the electrical properties of ALD-AZO films are closely related to the layer-by-layer structure because extrinsic doping would occur at/near the interfaces between the ZnO matrix and dopant layers.17 Figure 5a shows the increase of carrier concentration due to the doping \((\Delta n)\) as a function of the density of dopant layers \((m_{AlO})\). Herein, \( m_{AlO} \) was calculated by dividing the number of Al₂O₃ ALD cycles by the film thickness. As is clearly shown in Fig. 5a, \( \Delta n \) increased even until \( m_{AlO} \) reaches a value of \( 6.4 \times 10^6 \) cm⁻² when \( t_{TMA} \) is 0.1 s, while it exhibited the maximum value at a \( m_{AlO} \) value of \( 3.7 \times 10^6 \) cm⁻² in the surface-saturated condition \((t_{TMA} \geq 2 \text{ s})\). These results indicate that the decrease of \( N_{Al} \) resulted in the more uniform distribution of Al as schematically shown in Figs. 5b and 5c. In addition, it is clear that the higher carrier concentration for the reduced \( t_{TMA} \) value is due to the insertion of more dopant layers.

Another thing to be noted is that the AZO films deposited with the reduced \( t_{TMA} \) value could include more dopant layers until the carrier concentration reached the maximum value. To understand this, we developed the effective field model for doping as schematically given in Fig. 6.17 Due to the extrinsic doping, charged donors (blue dots) would be formed at/near the dopant layers. These donors can exert the effective field (red spheres) which suppresses the additional doping within that field due to the repulsion forces between adjacent donors or electrons orbiting those donors. In other words, these effective fields could determine the areal density of donors in an individual dopant layer. When the interval between dopant layers \( l \) becomes smaller, the effective field in the adjacent dopant layers is superposed. That is, the repulsion force between the donors in the adjacent layers becomes dominant and doping in a separate dopant layer is inhibited. In this geometric model, the minimum interval between dopant layers corresponds to a planar spacing between charged donors \( (d) \) and the diameter of the effective field as in Fig. 6 rather than just comparing that to the characteristic Debye length (<0.5 nm in the carrier concentration above \( 10^{20} \) cm⁻³). Herein, \( d \) can be simply calculated as \( d = (Z/N_l)^{1/2} \) where \( Z \) is the charge number of the donors and \( N_l \) is the areal density of generated carriers by incorporation of a single dopant layer as follows

\[
N_l = \frac{\Delta n}{m_{AlO}} = \frac{n_{AlO} - n_{ZnO}}{m_{AlO}} \tag{3}
\]

Equation 3 indicates that \( N_l \) at a \( t_{TMA} \) of 0.1 s is higher (\( \sim 6.9 \times 10^{13} \) cm⁻²) than that of the surface-saturated condition (\( \sim 4.5 \times 10^{13} \) cm⁻², \( t_{TMA} \geq 2 \text{ s} \)). In other words, more free electrons, and thus donors, are formed by reducing \( t_{TMA} \). If all donors are doubly charged \((Z = 2)\), via intake of oxygen from the ZnO by the incorporated Al dopants and subsequent formation of \( V_{Zn}^{2+}/Zn^{2+} \), \( d \) at a \( t_{TMA} \) of 0.1 s is about \( \sim 1.7 \) nm, which is smaller than that of the surface-saturated condition \((\sim 2.2 \) nm\). This indicates that the minimum intervals in the cases of the reduced \( t_{TMA} \) are much smaller compared to the surface-saturated condition \((t_l < l_a \) in Fig. 6). Therefore, it is believed that the decrease of \( t_{TMA} \) leads to the insertion of more dopant layers.

**Conclusions**

The effects of the Al distribution on the electrical properties of ALD-AZO films were investigated. The areal density of Al atoms in a single dopant layer was controlled by varying the pulsing time of TMA. By reducing the TMA pulsing time from 2 to 0.1 s, the resistivity of the ALD-AZO films decreased from \( 3.2 \times 10^3 \) to \( 1.7 \times 10^3 \) Ω cm. This decrease was attributed to the remarkable increase of the carrier concentration from \( 1.4 \times 10^{20} \) to \( 4.7 \times 10^{20} \) cm⁻³. It is believed that the increase of the carrier concentration is...
due to both the improved doping efficiency (from 13 to 58%) and the possibility of inserting more dopant layers within the ZnO matrix. Finally, it should be emphasized that this work suggests a direction of improving the conductivity of ALD-TCO films and a good methodology to investigate a doping mechanism of TCOs.

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References