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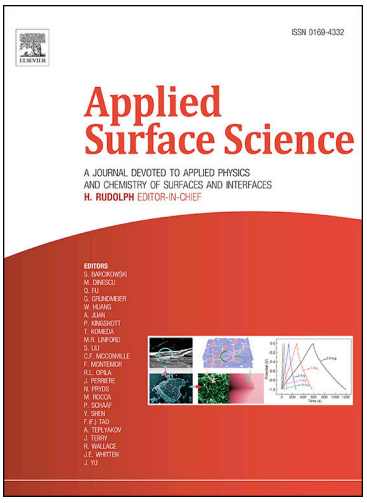

Full Length Article

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S. Kinnunen, K. Arstila, T. Sajavaara

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Al_2O_3 ALD films grown using TMA + rare isotope $^2H_2^{16}O$ and $^1H_2^{18}O$ precursors

S. Kinnunen[1], K. Arstila[1] and T. Sajavaara[1]

[1] *University of Jyvaskyla, Department of Physics, P. O. Box 35, FI-40014 University of Jyvaskyla, Finland*

Abstract

In this work hydrogen and oxygen migration and exchange reactions in the atomic layer deposited (ALD) Al_2O_3 thin films were studied together with hydrogen incorporation by varying deposition parameters. Al_2O_3 films deposited at low temperatures can contain more than 20 at. % of hydrogen. Both higher temperature and longer purge length decrease the hydrogen and carbon concentrations significantly. In order to track the hydrogen and oxygen movement in the films, heavy water ($^2H_2^{16}O$) and oxygen-18 enriched water ($^1H_2^{18}O$) were used as precursors in combination with trimethylaluminium (TMA). Different isotopes of the same element were quantified by means of time-of-flight elastic recoil detection analysis (ToF-ERDA). It was found out that $^1H/^2H$ exchange reactions take place even at room temperature if the hydrogen concentration is high enough. On the other hand, oxygen atoms in the films do not migrate notably.

Keywords: ALD, Al_2O_3, Low temperature, Heavy water, Hydrogen migration, TMA

1. Introduction

Atomic layer deposited (ALD) amorphous aluminium oxide (Al_2O_3) is both extensively used and much studied thin film material. Alumina films have been studied, for example, as a high-k material for semiconductor industry [1–3] as well for gas permeation barriers [4–6]. There are numerous ALD processes for Al_2O_3 but especially the process with trimethylaluminium (TMA) and water as precursors is widely studied (www.atomiclimits.com ALD database mentions almost 300 articles as to date [7]) and the reaction mechanism is also believed to be quite well understood [8, 9].

One early identified application for amorphous ALD-oxide films has been to use it for moisture and gas permeation barriers [10]. Thin moisture barriers are needed in packaging materials where flexibility of the barrier is of importance. Another example is organic light emitting diodes (OLED) which require transparent moisture barrier. OLEDs are known to be sensitive to water vapour and oxygen, and in order to increase their lifespan diffusion of these gases must be prevented [11]. When considering gas and moisture barriers, atomic layer deposition is an ideal deposition method. Due to the self terminating reactions of ALD, conformal and pinhole-free films can be grown even on complex and porous substrates [12, 13]. It is also possible to deposit the ALD-films at low temperatures required by the organic substrates. Therefore coating polymers with the ALD is an attractive option.

ALD thin films often contain significant amounts of hydrogen, especially when grown at low deposition temperatures. In addition to water vapour [4] and oxygen [6], also hydrogen can cause degradation for example in capacitors components [14]. Al_2O_3 thin films along with other ALD-oxides have

been studied as H_2 barriers for this purpose and it has been shown that the diffusion of hydrogen to a capacitor dielectric material decreases significantly if a protective ALD film is applied [15]. However, in some applications hydrogen is a desirable element in the film. Hydrogen from the ALD capping film can, for example, passivate the Si-interface in solar-cells by binding to dangling bonds which are responsible for the charge carrier recombination resulting in suboptimal energy conversion efficiency [16].

Metal-organic ALD precursors are frequently used and the organic ligands very often contain hydrogen. In addition, hydrogen containing coreactants such as ^1H_2O and NH_3 are extensively used for depositing oxides and nitrides, respectively. Therefore hydrogen is a common impurity in all thin films but it is quite often disregarded because only a few measuring techniques, such as elastic recoil detection analysis (ERDA) and secondary ion mass spectrometry (SIMS), can directly detect hydrogen atoms in the films. The advantage of ERDA and especially time-of-flight ERDA (ToF-ERDA) over SIMS is the possibility of quantative elemental depth profiling [17].

For example in the case of TMA and ^1H_2O process both precursors contain hydrogen that can be incorporated in the film. Al_2O_3 can be deposited from the TMA and water at as low as 33 °C but the impurity contents are then very high [18]. In order to decrease the residual hydrogen concentration in Al_2O_3 films, one can increase the deposition temperature [19]. Alternatively, post deposition annealing can also be used to decrease the hydrogen content [20]. On the other hand, many of the applications requiring gas barriers involve polymers or other organic substrates and elevated temperatures can not be used during or after the deposition.

The use of precursors containing rare stable isotopes can give information not only on reaction mechanism but also on sources of impurities in the films. For example, hydrogen has two stable isotopes, ^{1}H (99.985 %) and ^{2}H (0.015 %) [21] and in the following text hydrogen refers to ^{1}H and deuterium to ^{2}H. Similarly, water refers to $^{1}H_2O$ and heavy water to $^{2}H_2O$.

Deuterated precursors have been used in various studies [9, 19, 22, 23]. By using heavy water instead of water in TMA + $^{1}H_2O$ process the source of hydrogen impurity can be detected. It is often presumed that as the elements do not change, heavy water can be treated as equivalent to normal water [9, 24, 25].

These isotope studies have given detailed information on reaction mechanism and TMA + H_2O process [9, 19, 25] is probably the most widely studied ALD process. That said, even the reason of the most important aspect of ALD – the self terminating reaction – in the case of this process is still under debate. Saturation of the reaction is often contributed to the steric hindrance of the ligands which populate the surface so that the reactive sites are blocked [9, 26]. On the other hand, Vandalon *et al.* propose that the steric hindrance can not be the sole cause of terminating reaction. Their claim is that non-reactive methyl groups cause reactions to stop at least in the lower temperatures [25]. However, there are open questions such as why the persistent -CH_3 groups are not incorporated in the film as a carbon impurity since the deposited films contain only a small concentration of carbon even at low deposition temperatures [25, 27].

In this work we studied how hydrogen is incorporated in the films. In addition, the migration of hydrogen (and oxygen) in the films is studied. In

order to do so, both heavy water (^2H_2O) and oxygen-18 (natural abundance 0.2 % [21]) enriched water ($H_2\,^{18}O$) were used as oxygen sources. The effect of different ALD conditions, such as the deposition temperature and purge lengths, were also studied. It was found that the impurities decrease with increasing deposition temperature. In addition, the migration of hydrogen was only detected if hydrogen concentration in the film was high.

2. Experimental details

Al_2O_3 films were deposited using Beneq TFS 200 side flow reactor. Nitrogen from Inmatec PN 1150 nitrogen generator (99.999 %) was used as a carrier gas as well as for purging between the precursor pulses. Pressure during the deposition in the reaction chamber was 1–2 mbar. TMA (Strem $>$ 98 %) was used as an aluminium source for the process. Three types of water were used as an oxygen source: normal water $^1H_2^{16}O$, heavy water $^2H_2^{16}O$ (Medical Isotopes Inc. 99.99 %) and oxygen-18 enriched water $^1H_2^{18}O$ (Medical Isotopes Inc. 97 %). Deposition temperature was varied between 70 °C and 250 °C. Pulse lengths for both precursors were kept constant at 300 ms which is double the time for our typical Al_2O_3 processes. The longer pulse length was used to ensure a complete saturation of the substrate surfaces. Purging time was in most depositions 10 s after both precursor pulses but the effect of the purging time was also investigated and then it was varied between 3 and 60 seconds. All films were deposited on n-type (100) silicon chips cut from a bigger wafer with native SiO_x layer. Sample pieces were distributed in front, back and sides of the reactor in order to ensure film conformality all over the reactor. To minimise H-contamination prior

the TMA + ^2H_2O deposition, the reactor was treated with 50 ^2H_2O pulses (150 ms).

As-deposited samples were also exposed to elevated temperature and humid conditions by storing them in a climate chamber (Weiss WK3-180/40) for 24 or 48 hours at 60 °C and in 80 % relative humidity (RH) at atmospheric pressure.

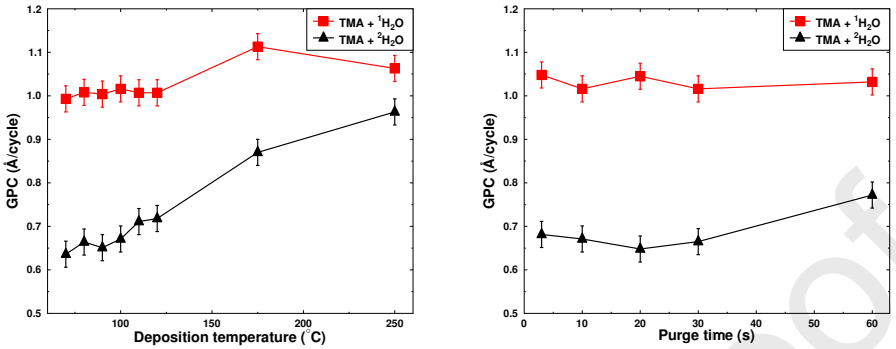
The elemental composition and depth profiles of the films were measured with a time-of-flight elastic recoil detection analysis (ToF-ERDA) using 11.915 MeV $^{63}Cu^{6+}$ ions [28]. Recoiled species were detected at 41° angle using mirror measuring geometry. Analysis and elemental depth profiles were made with Potku analysis software [29]. Surface and interface regions of the films were excluded from the elemental analysis and compositions were calculated from the bulk of the film.

Al_2O_3 films were investigated with helium ion microscopy (HIM) (Zeiss Orion Nanofab) in order to study the porosity of the films.

Thicknesses of the films were measured with Rudolph AUTO EL III ellipsometer with 632.8 nm laser.

3. Results and Discussion

The deposition rate decreases about one third when normal water is changed to ^2H_2O as seen in the Fig. 1a when every other parameter is kept constant. Similar decrease in growth-per-cycle (GPC) is reported by Hiraiwa *et al.* [24]. This is most probably due to the kinetic isotope effect, which is utilised for example in chemical reaction mechanism studies [30]. This effect raises the activation energy of the reaction and therefore reduces the reac-



(a) (b)

Figure 1: a) Growth-per-cycle as a function of the deposition temperature. Films were deposited using 300 ms precursor pulses and 10 s N_2 purges between the pulses. b) Growth-per-cycle of the films deposited at 100 °C. Nitrogen purge was varied between 3 and 60 s.

tion rate which could explain the results. As mentioned in the Introduction, the interchangeability of ^1H_2O and ^2H_2O is often assumed. On the other hand, one can not rule out that the changes in activation energies can also change the probabilities of different reaction paths making some paths more favourable than others compared to situation with normal water. For example reaction with the TMA and oxygen bridge site (i.e. Al–O–Al) [31] does not involve deuterium which may favour this reaction route if the reaction rate with O^2H-groups is decreased.

The GPC of the TMA + ^1H_2O process has been reported to increase as a function of the deposition temperature having the highest GPC at 200–300 °C depending on the source [22, 24, 32, 33]. Our results are compareable and the growth rate starts to decrease between 200 and 250 °C (Fig. 1a). This has been attributed to the decrease of reactive OH-sites due to dehydration

[25, 33]. On the other hand, deposition with ^2H_2O changes the situation so that the growth rate continues to increase even at 250 °C and approaches then the GPC of the ^1H_2O process. It seems that the extra energy from the higher temperature drives the reaction more than what the dehydration slows it. When considering purging times (Fig. 1b), it seems that the purging length does not play a significant role in ^1H_2O process at 100 °C, but longer purging increases the GPC slightly in ^2H_2O process. This is another indication of slower reaction rates due to the isotope effect.

Composition and elemental depth profiles of the samples were produced from coincidence time-of-flight and energy data (Fig. 2). Elemental composition of all the samples can be found in Supplementary (Table A.1 and A.2).

Al_2O_3 films grown at low temperatures tend to have oxygen rich composition and the O/Al ratio closes to the stoichiometric value of 1.5 only at 200 °C and above [9, 18, 34]. Our similar results are shown in Fig. 3a. Also purging time changes the O/Al ratio of films deposited at 100 °C (Fig. 3b) although even the 60 s long purging time produces O-rich film. Even though the GPC decreases when the oxygen source is changed from ^1H_2O to ^2H_2O (Fig. 1a), it does not affect the ratio between the main components of the film. In this regard, using ^2H_2O instead of ^1H_2O is well justified.

While O/Al ratio is independent of the oxygen precursor, there is a difference in the amount of hydrogen incorporated in the films (Fig. 4a). Films deposited with heavy water tend to have slightly higher total amount of ^1H and ^2H compared to hydrogen content in the films deposited with normal water. In earlier studies the equivalence between the use of ^1H_2O or ^2H_2O have

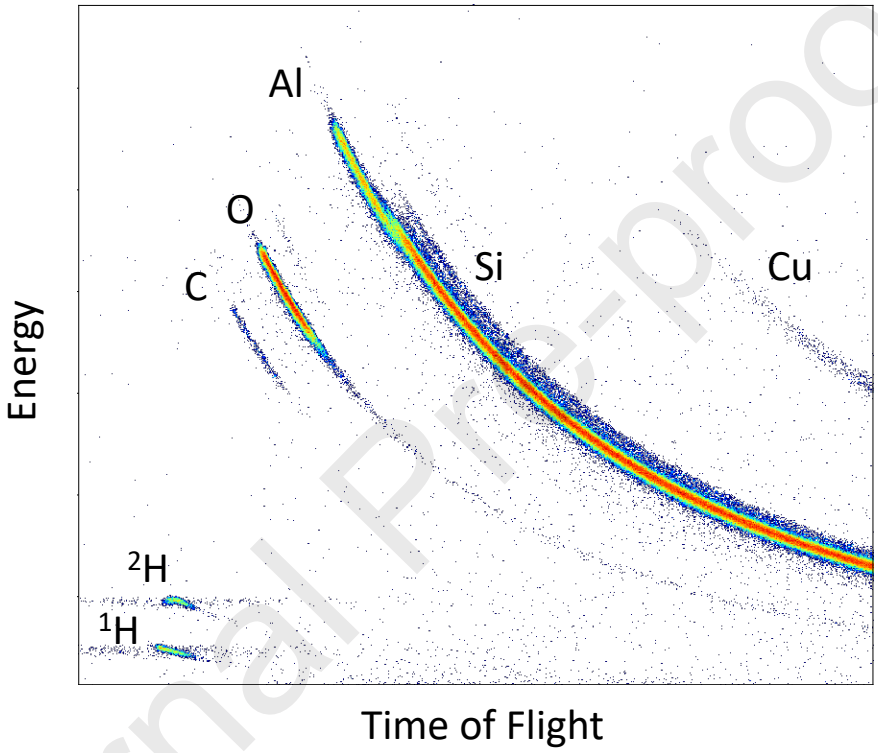
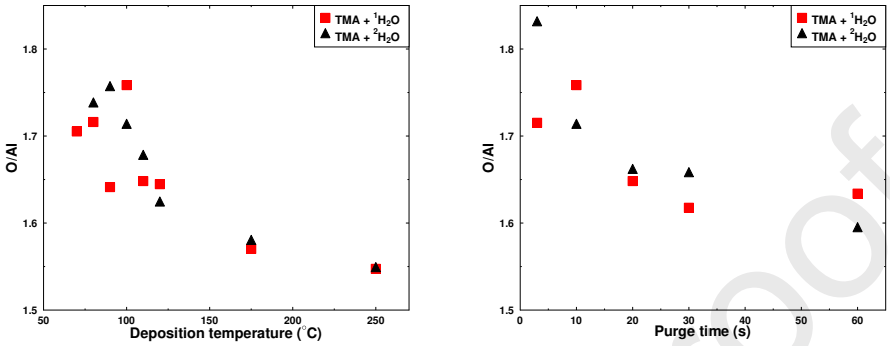
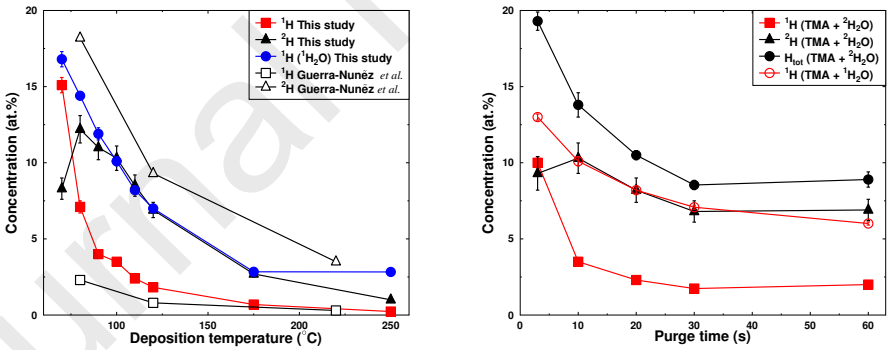


Figure 2: Coincidence time-of-flight and energy histogram of a ToF-ERDA measurement. Elements and isotopes differentiate according to their masses. Film was deposited using 1000 cycles of TMA and $^{2}H_2O$ at 100 °C. Scattered ^{63}Cu beam used for the measurement is also visible.



(a) (b)

Figure 3: a) O/Al ratio as a function of the deposition temperature. Samples were deposited using 300 ms precursor pulses and 10 s purging. b) O/Al ratio as a function of the purging time. Samples were deposited at 100 °C.



(a) (b)

Figure 4: a) ^1H and ^2H impurity concentrations at different deposition temperatures. Films were deposited using 300 ms precursor pulses and 10 s purging times. Comparison to Guerra-Nunẽz *et al.* [9] is also shown. b) ^1H and ^2H concentrations as a function of purge time. Deposited at 100 °C using 300 ms precursor pulses.

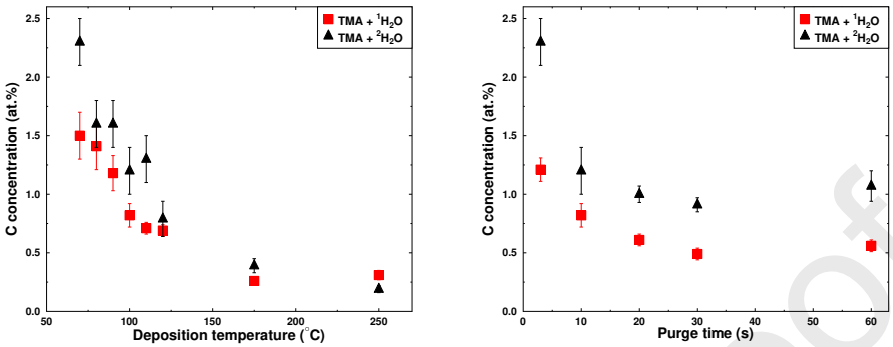
been justified by similar total hydrogen concentrations [9, 19]. Somewhat similar results to ours, with higher total hydrogen when ^1H_2O was replaced with ^2H_2O, were obtained by Hiraiwa *et al.* [24]. However, their conclusion was that the difference is not significant and can be neglected. Nevertheless, the total hydrogen concentration follows a similar trend with both oxygen precursors even though the use of ^2H_2O results in somewhat higher total hydrogen concentration than ^1H_2O.

The deposition temperature plays a major role in hydrogen incorporation in ALD-Al_2O_3 films. At high temperatures the hydrogen concentration decreases as shown in Fig. 4a and goes below 5 at. % only above 175 °C. The main hydrogen source is from water since there is more deuterium than hydrogen in the film when the deposition temperature is higher than 70 °C. It is notable that in our study the majority hydrogen isotope changes from hydrogen to deuterium between 70 and 80 °C. Films deposited at 70 °C, based on visual inspection as well as with thickness profiles given by the ellipsometer, appeared completely fine; films were uniform in thickness all around the reactor and visually looked similar to ones deposited at higher temperatures. When the deposition temperature was decreased to 60 °C clear signs of CVD-growth were observed (See Supplementary A.7) for the TMA + ^2H_2O process. Films deposited with ^1H_2O were uniform. The drastic change in ^1H and ^2H composition at 70 °C would therefore be an indication of CVD component in the reaction. It is known [18] that water molecules physisorpt to "cold" surfaces and require long pumping (i.e. purging) time. If the purging time is not sufficient, physisorption leads to higher than monolayer surface concentration of ^1H_2O or OH which is still present when TMA is pulsed to

the reactor. However, as seen in Fig. 4a, the deuterium concentration drops significantly at 70 °C, indicating that deuterium from water is not incorporated in the film in large quantities. In addition, CVD-growth would increase the GPC which was not observed at 70 °C (Fig. 1a). This can be explained by the studies of Vandalon *et al.* [22, 25] where they showed that there is a certain temperature limit where water is not reactive enough towards the CH_3-groups at the substrate surface which leaves excessive amount of persistent CH_3-groups in the film. As Vandalon *et al.* pointed out, also simulations suggest that the isolated CH_3-groups have higher reaction barrier compared to the multiple methyl groups in close proximity to each other [35]. These isolated unreactive methyl groups could be the source of the high hydrogen concentration in the film deposited at 70 °C.

As seen in Fig. 5a and 5b, the carbon concentration follows very similar trend to the hydrogen concentration and decreases with the increasing deposition temperature and purge length. Carbon concentration is not high even at low temperatures and the use of ^2H_2O instead of ^1H_2O does not have a significant effect on carbon concentration. However, it remains as an open question what happens to the carbon since even at 70 °C the amount of carbon in the films is only 2.3±0.2 at.% (Fig. 5a). If hydrogen would be in the film in the form of methyl groups we should expect carbon concentration to be closer to 5 at.%. Same observation was done by Vandalon *et al.* and they proposed that these methyl groups can react with water in subsequent cycles.

Comparison of ^1H and ^2H impurities with previous work by Guerra-Nunẽz *et al.* is made also in Fig. 4a. General trends are similar although our



(a) (b)

Figure 5: a) Carbon concentration of films deposited at different temperatures using 300 ms pulses and 10 s purging times. b) Carbon concentration as a function of purging times, films were deposited at 100 °C using 300 ms pulses.

results show slightly higher deuterium content but somewhat lower hydrogen incorporation. All our samples in Fig. 4a are deposited with 300 ms precursor pulses and 10 s N_2 purges while Guerra-Nunẽz *et al.* used 1 s pulses, 2 s exposure time and 60 s purging. While this long ALD cycle can improve the film quality, it also makes the deposition very long and maybe impractical for industrial purposes.

The length of the purge has a significant effect on the hydrogen incorporation in the film as seen in Fig. 4b. Both the hydrogen and deuterium concentration decrease as the purging times increases. Although deposited films are conformal in thickness (less than 2 % variation over the area of the reactor) even with the shorter purging times, and therefore seem to represent pure and self-limiting ALD-growth, the films are far from identical. Reactions are observed to go to completion at quite slow rate at low temperatures, requiring 30 s purging even as high as at 100 °C before the hydrogen

concentration saturates. Similar trend is observed for ^1H_2O process which is somewhat surprising since the GPC does not change with increasing purging times (Fig. 1b).

The mass gain per cycle is a more direct indication of slow reaction rate and desorption of reaction species at low temperatures compared to measuring only GPC, as films with similar thickness can have different mass density. It is shown on quartz crystal microbalance (QCM) studies that the mass gain per cycle decreases as the purging times are increased at low temperatures [18, 36]. In addition, the mass loss after the precursor pulse can continue for tens of seconds indicating that the reactions are slow and the desorption of reaction products and physisorbed surface species require long purging times at low temperatures. This supports our finding that long purging times decrease hydrogen, carbon and excess oxygen content in the film.

This purging time issue is one example of a sources of inconsistency in ALD research pointed out by Sønsteby *et al.* in the recent paper [37]. They address the problems on ALD reproducibility and relate, for example, higher than expected GPC to short purging times possibly leading to CVD like growth. This is all true, but looking only at the GPC does not guarantee that the results are comparable as we have shown above. Even if purging times are adequate to produce conformal films, purging can be short enough to also change the composition of the film as seen in Figure 4b even if the GPC does not change (See Fig. 1b). In addition, the reactor used will influence the required purging (and pulsing) times. Details, such as vacuum level, reactor geometry and gas flows will have an effect on deposition and film growth. It is important to note this issue when comparing the results obtained by the

different groups. This issue is most pronounced at low temperatures. As seen in Fig. 4a, our results are somewhat different compared to those measured by Guerra-Nunẽz *et al.* The difference between our and their results is of order of a few at.% which is larger than the margin of error. Therefore the discrepancy must come from the different pulsing and purging times, reactor geometry and deposition pressure, and it is important to report all the deposition parameters in order to compare the results reliably.

We also studied the hydrogen migration in the Al_2O_3 films. A depth profile of an as-deposited TMA + ^2H_2O film is presented in Figure 6a). The films were deposited using 150 ms precursor pulses and 3 s purging at 100 °C which makes them hydrogen rich. In figure 6b) the same film is shown after 24 h exposure in a climate chamber. The conditions in the chamber were kept constant at 60 °C and at 80 % relative humidity. After the treatment the deuterium concentration was dramatically decreased and at the same time the concentration of ^1H had increased equally keeping the total amount of elemental hydrogen constant. This can be explained by the hydrogen exchange reactions. Hydrogen in water vapour and gaseous H_2 can exchange hydrogen atoms with the impurity hydrogen/deuterium in the film. Since the natural abundance of deuterium (0.02 %) is much lower than the ratio in these films, the percentage of the ^2H drops due to these exchanges. Interestingly, the exchange does not happen only at the surface but also all the way through the 80 nm thick films. This requires migration of hydrogen for rather long distances even in these low temperature annealing conditions. Other possibility is that the film is porous and gases penetrate the film easily.

However, there is a threshold for hydrogen concentration that is needed

for the exchange reaction to proceed through the whole film. Sample deposited at 100 °C with 300 ms pulses and 10 s purging times contain ~ 15 at.% of total hydrogen (^{1}H + ^{2}H). When this sample is exposed to climate chamber conditions, there are no major changes in either hydrogen or deuterium concentrations (See Supplementary A.9).

We can observe in Fig. 6a that both ^{1}H and ^{2}H are unevenly distributed in the film. There is more ^{1}H at the surface and more ^{2}H at the interface. This is an example of a similar exchange reaction that happens also at room temperature in air given enough time (1 day) between the deposition and characterization (see Supplementary Fig. A.8). Therefore data shown in Figures 1, 3, 4 and 5 were measured from the samples that were kept in a load-lock under a vacuum condition (< 1 mbar) until exposed to air very briefly just before the characterization.

It is known based on IR-studies that the hydrogen impurities in ALD-Al_2O_3 films are found at least in the form of OH-groups [38, 39]. Signal from OH stretching has been shown to increase as the hydrogen content of the film increases, supporting the claim that hydrogen is found in the films in form of OH-groups [38]. Films deposited at low temperature are also oxygen rich hinting that there are undercoordinated oxygen atoms. Relatively low carbon concentration rules out the speculation that the majority of the hydrogen would be in the form of CH_3-groups. Furthermore, in the films grown with TMA + ^2H_2O, ^{2}H atoms are most likely bound to oxygen as they originate from the water.

In order to see if the hydrogen migration is related to the movement of the whole OH-group or if there is any oxygen diffusion from the ambient

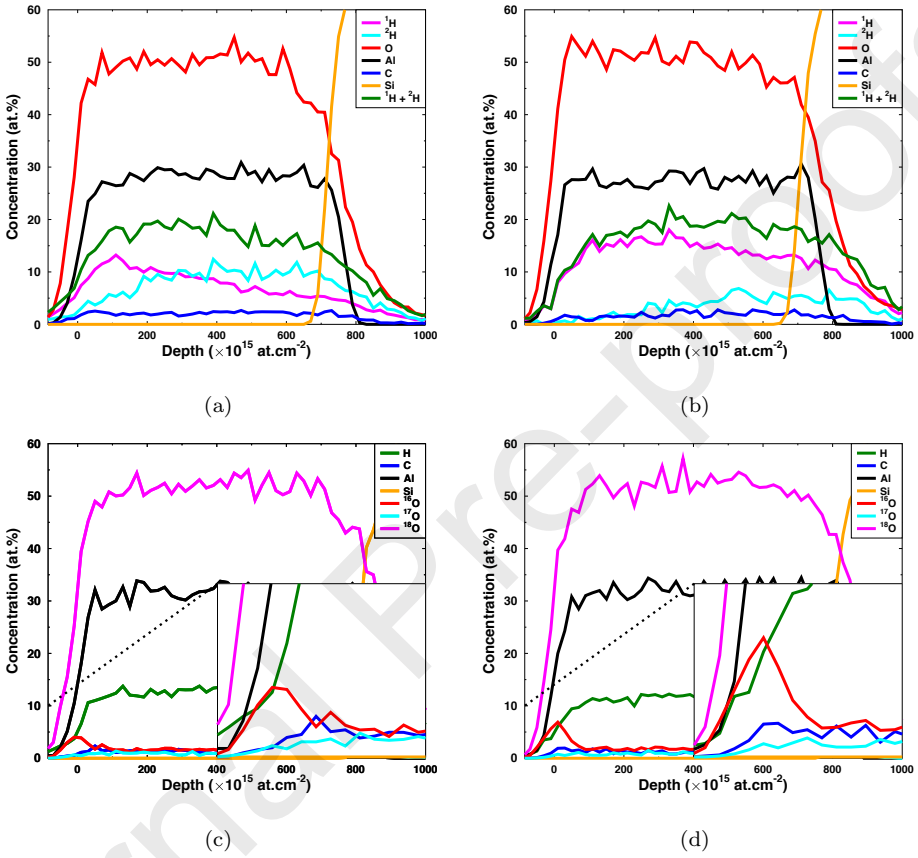


Figure 6: Elemental depth profiles of Al_2O_3 films deposited at 100 °C with 150 ms precursor pulses and 3 s purging. a) As-deposited film using TMA and ^2H_2O. The sample was kept at room temperature in air for one day before the characterization. b) The same film as in a) but after 24 h at 60 °C and 80 % RH. c) As-deposited film using TMA and $H_2^{18}O$. The sample was kept for one day at room temperature in air before the characterization. d) The same film as in c) but after 48 h in 60 °C and 80 % RH.

present, films using TMA and $H_2^{18}O$ as precursors were deposited. The depth profile of an as-deposited film grown at 100 °C is presented in Fig. 6c). We see that oxygen-18 enriched water produces films that contain less hydrogen than the films deposited with ^2H_2O. However, hydrogen concentration in Fig. 6c is comparable to the samples deposited with ^1H_2O. This is expected since small change in oxygen mass does not have a great effect on the activation energy and therefore kinetic isotope effect is not noticeable. After 48 h in the climate chamber at 60 °C and at 80 % RH the films show only very minor difference at the surface as seen in Figure 6d). Inside the film the amount of oxygen-18 does not change, indicating that oxygen even in OH-groups can not efficiently exchange with oxygen from O_2 or H_2O at similar rate compared to hydrogen. This indicates that only hydrogen is migrating in the film, not whole OH-groups. From the results it is also clear that the oxygen that is bonded to aluminium does not exchange with oxygen atoms from O_2 or ^1H_2O molecules.

Dingemann *et al.* showed that hydrogen effuses from the Al_2O_3 films in the form of both H_2 and ^1H_2O when annealed at 200 to 1000 °C in high vacuum (10^{-7} mbar) conditions [20]. That process, however, must be different compared to process reported in this paper. The high temperature annealing removes and so decreases the amount of hydrogen in the films. Here we observe only an (isotope) exchange reaction and the total amount of hydrogen in the film does not change. Considering that the $^1H/^2H$-exchange reaction is chemically similar to the H/H-exchange, it is clear that the hydrogen moves through the films easily if the film has been deposited at low temperature and has high hydrogen content. Hydrogen diffusion studies done

by Cameron *et al.* with radioactive hydrogen isotope tritium (^{3}H) show that hydrogen can diffuse through also in atomic form [40], which is in agreement with our findings.

Porosity of the film could increase both the efficiency of the hydrogen exchange and hydrogen permeation in the film enabling gases to penetrate and interact also deeper in the film. Many amorphous ALD films are known to be pinhole free [4, 41] and this was confirmed also here with helium ion microscopy (HIM) (See Supplementary A.10a and A.10b). With the nominal HIM resolution of 0.5 nm no detectable porosity could be observed.

4. Conclusions

Although ALD alumina films have been suggested and used as possible gas barriers, it is clear that at least hydrogen is able to transport through the film rather easily in a warm and humid environment if the initial hydrogen concentration of the film is high. Our results indicate that the hydrogen transport proceeds via hydrogen exchange reactions. Therefore it is possible to decrease the hydrogen transport by controlling the amount of hydrogen left in the film during the deposition. This can be achieved by careful selection of precursors or increasing the deposition temperature and using very long purging times. Optionally also post-deposition annealing can be applied. However, the coated material in barrier applications is commonly a polymer, which many times rules out high deposition temperatures. Longer purges in turn increase the deposition times, possibly by an order of magnitude, which reduces the throughput significantly making the ALD-Al_2O_3 films as hydrogen permeation barriers not so attractive method.

As demonstrated here, a significant amount of hydrogen is stored in the films and hydrogen can also move through the film if the concentration is high. Oddly enough, this could open opportunities using ALD-Al_2O_3 films as proton conductors [42]. ALD also offers various ways to control the hydrogen content and diffusion.

In order to study the hydrogen incorporation in the films, we replaced ^1H_2O with ^2H_2O. Change of isotope in a molecule should not change the chemistry since the element is not changed. However, in the case of hydrogen, replacing hydrogen with deuterium doubles the mass of the atom and it affects the film growth. Growth per cycle is decreased and impurity carbon and total hydrogen incorporated in the film is increased when ^2H_2O is used. On the other hand, the ratio between the main components, oxygen and aluminium, is independent of oxygen precursor. While there are differences in the films depending on the oxygen precursor, the general trends are similar and therefore the comparison is justified when done carefully.

It is also noteworthy to keep in mind that in addition to pulsing times and deposition temperature, purging times affect greatly the film quality and this should be taken in to account especially when comparing results from different studies. Our work clearly demonstrates that even though a quick glance at the samples does not show any difference, there can be a significant difference in the compositions. If this is the case even with the close to "ideal" ALD process of TMA and water, even more care should be taken when interpreting results obtained with limited characterization techniques from more demanding processes.

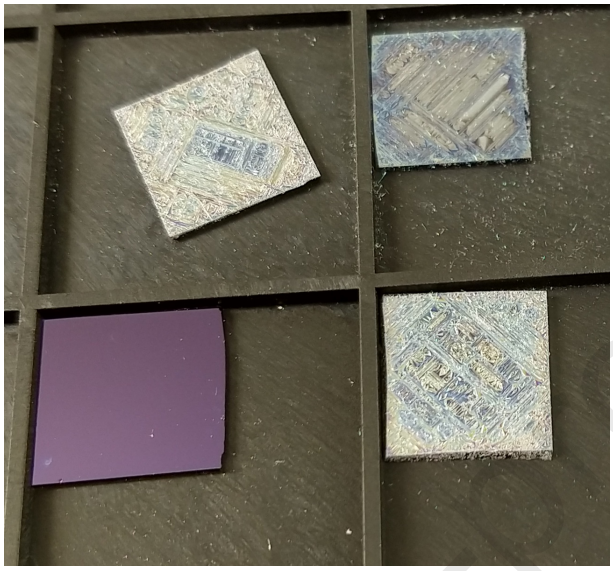


Figure A.7: Uncontrolled CVD-growth on three silicon chips (TMA + ^2H_2O) and one sample with proper film (TMA + ^1H_2O). All samples were deposited at 60 °C with 300 ms pulses and 10 s purging.

Appendix A. Supplementary

When the purging times are too short and there is a substantial amount of previous precursor available when the next precursor is introduced to reactor, growth is not under control and we experience CVD-like growth (Fig. A.7). The film is also much thicker than what would be expected for the ALD-growth.

If films are not properly stored, the hydrogen exchange reactions take place also at room temperature as seen in Fig. A.8. As the concentration of deuterium decreases over time, the concentration of hydrogen increases. The total amount of ^1H + ^2H increases slightly but the change is not significant.

However, there seems to be a threshold value for hydrogen exchange re-

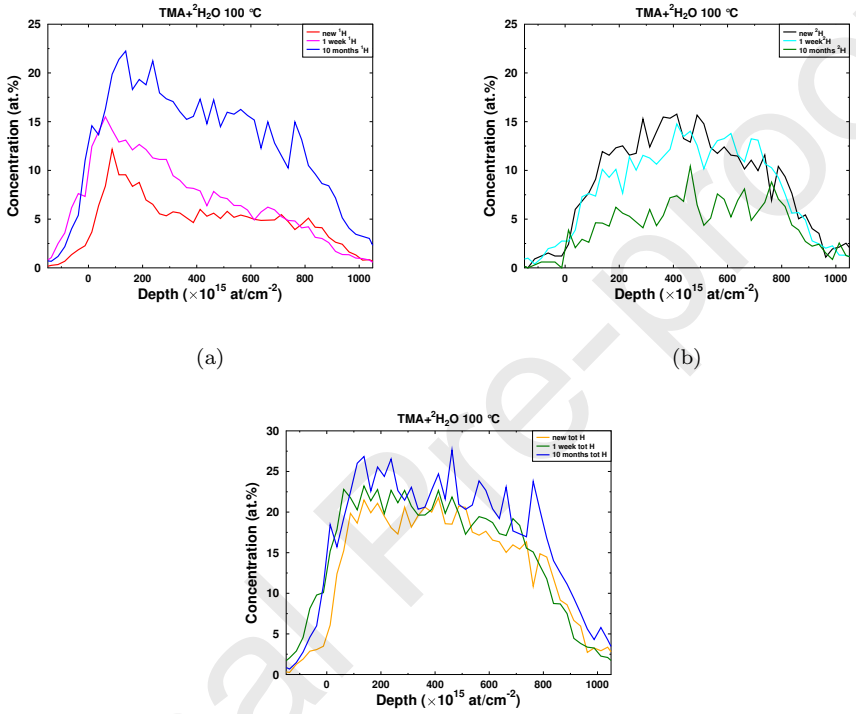


Figure A.8: The sample was deposited at 100 °C using 150 ms pulses and 3 s purging making the hydrogen concentration high. The sample was stored in ambient condition and measured again later. The ^{1}H concentration increased as the ^{2}H concentration decreased equally. a) Elemental depth profile of ^{1}H, b) ^{2}H and c) the sum of ^{1}H and ^{2}H presented in a) and b).

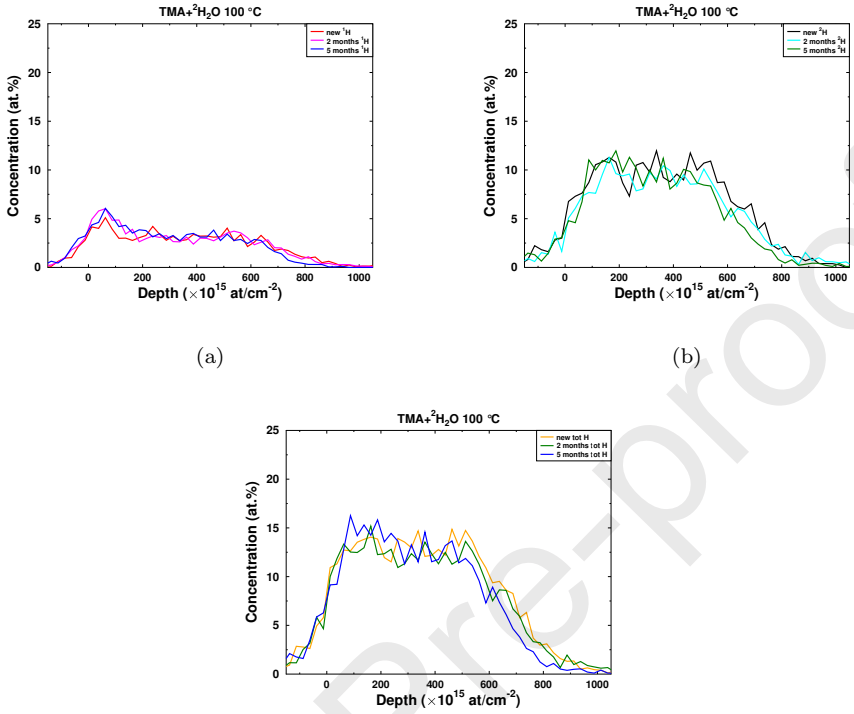
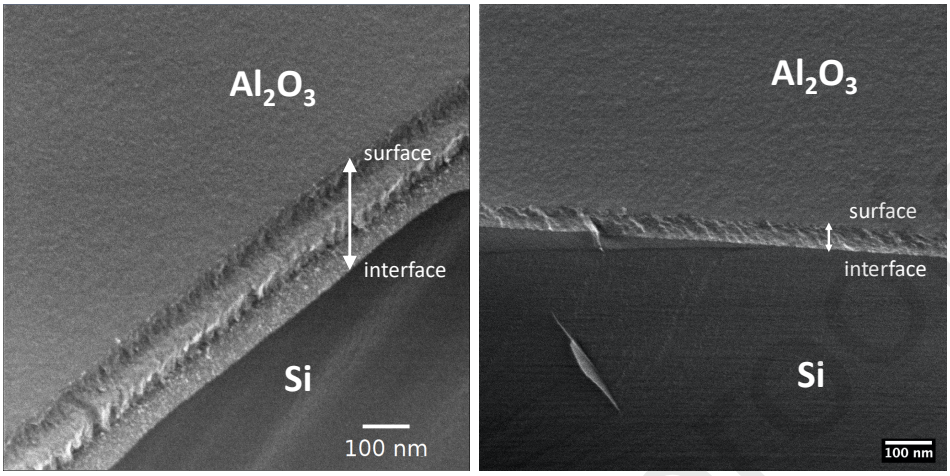


Figure A.9: The sample was deposited at 100 °C using 300 ms pulses and 10 s purging and was stored in ambient conditions and measured again later. a) Elemental depth profile of ^{1}H, b) ^{2}H and c) the sum of ^{1}H and ^{2}H presented in a) and b).

action. If longer purging times are used, resulting lower hydrogen content, there is no significant change in hydrogen or deuterium content when samples are stored in air as seen in Fig. A.9.

The cross section of an Al_2O_3 film is seen HIM micrograph (Fig A.10) tilted in 30° angle. Micrograph shows a pinhole free surface. However, HIM does not resolve any sub-nanometer porosity.

In Table A.1 are listed the elemental compositions of the films in tem-



(a) (b)

Figure A.10: Cleaved 100 nm thick Al_2O_3 film at 30° angle imaged with HIM. a) The film was deposited with TMA and ^2H_2O at 100 °C using 150 ms precursor pulses and 3 s purging. b) The film was deposited with same recipe as in a) but using TMA + $^1H_2{}^{18}O$.

perature series and in Table A.2 are the elemental compositions of the films deposited at 100 °C with varying purge lengths.

Table A.1: Elemental composition of the films deposited at different temperatures. The films were deposited using TMA and $^1H_2O/^2H_2O$ with 300 ms pulses and 10 s purging.

T(°C)	Al	O	C	^{1}H	^{2}H
TMA + ^2H_2O					
70	25.9±0.6	48.5±0.9	2.3±0.2	15.1±0.5	8.3±0.7
80	28.9±0.7	50.2±1	1.6±0.2	7.1±0.4	12.2±0.9
90	30.3±0.7	53.2±1	1.6±0.2	4±0.2	11±0.8
100	31.3±0.7	53.6±1	1.2±0.2	3.5±0.2	10.3±0.8
110	32.8±0.7	55±1	1.3±0.2	2.4±0.2	8.5±0.7
120	34.5±0.6	56±0.9	0.79±0.11	1.82±0.15	6.9±0.5
175	37.3±0.4	58.9±0.6	0.39±0.05	0.69±0.06	2.7±0.2
250	38.7±0.4	59.9±0.6	0.19±0.03	0.23±0.03	1±0.13
TMA + ^1H_2O					
70	30.2±0.6	51.5±0.9	1.5±0.2	16.8±0.5	-
80	31±0.3	53.2±0.4	1.41±0.07	14.4±0.2	-
90	32.9±0.7	54±0.9	1.18±0.15	11.9±0.4	-
100	32.3±0.5	56.8±0.8	0.82±0.1	10.1±0.3	-
110	34.4±0.2	56.7±0.3	0.71±0.04	8.2±0.11	-
120	34.9±0.3	57.4±0.4	0.69±0.05	7±0.14	-
175	37.7±0.3	59.2±0.5	0.26±0.03	2.84±0.1	-
250	38±0.3	58.8±0.5	0.31±0.04	2.83±0.1	-

Table A.2: Elemental composition of the films deposited with different purging times. The films were deposited using TMA and $^{1}H_2O/^{2}H_2O$ with 300 ms pulses at 100 °C.

TMA + $^{2}H_2O$					
Purge (s))	Al	O	C	^{1}H	^{2}H
3	27.7±0.6	50.7±0.8	2.3±0.2	10±0.4	9.3±0.6
10	31.3±0.7	53.6±1.0	1.2±0.2	3.5±0.2	10.3±0.8
20	33.3±0.3	55.3±0.5	1±0.07	2.3±0.09	8.2±0.3
30	34.1±0.3	56.5±0.4	0.91±0.06	1.74±0.07	6.8±0.3
60	34.7±0.6	55.3±0.9	1.07±0.13	2±0.13	6.9±0.5
TMA + $^{2}H_2O$					
3	31.6±0.2	54.2±0.3	1.21±0.05	13±0.2	-
10	32.3±0.5	56.8±0.8	0.82±0.1	10.1±0.3	-
20	34.4±0.3	56.7±0.5	0.61±0.05	8.2±0.2	-
30	35.3±0.3	57.1±0.4	0.49±0.04	7.08±0.13	-
60	35.5±0.2	58±0.3	0.56±0.03	6.01±0.1	-

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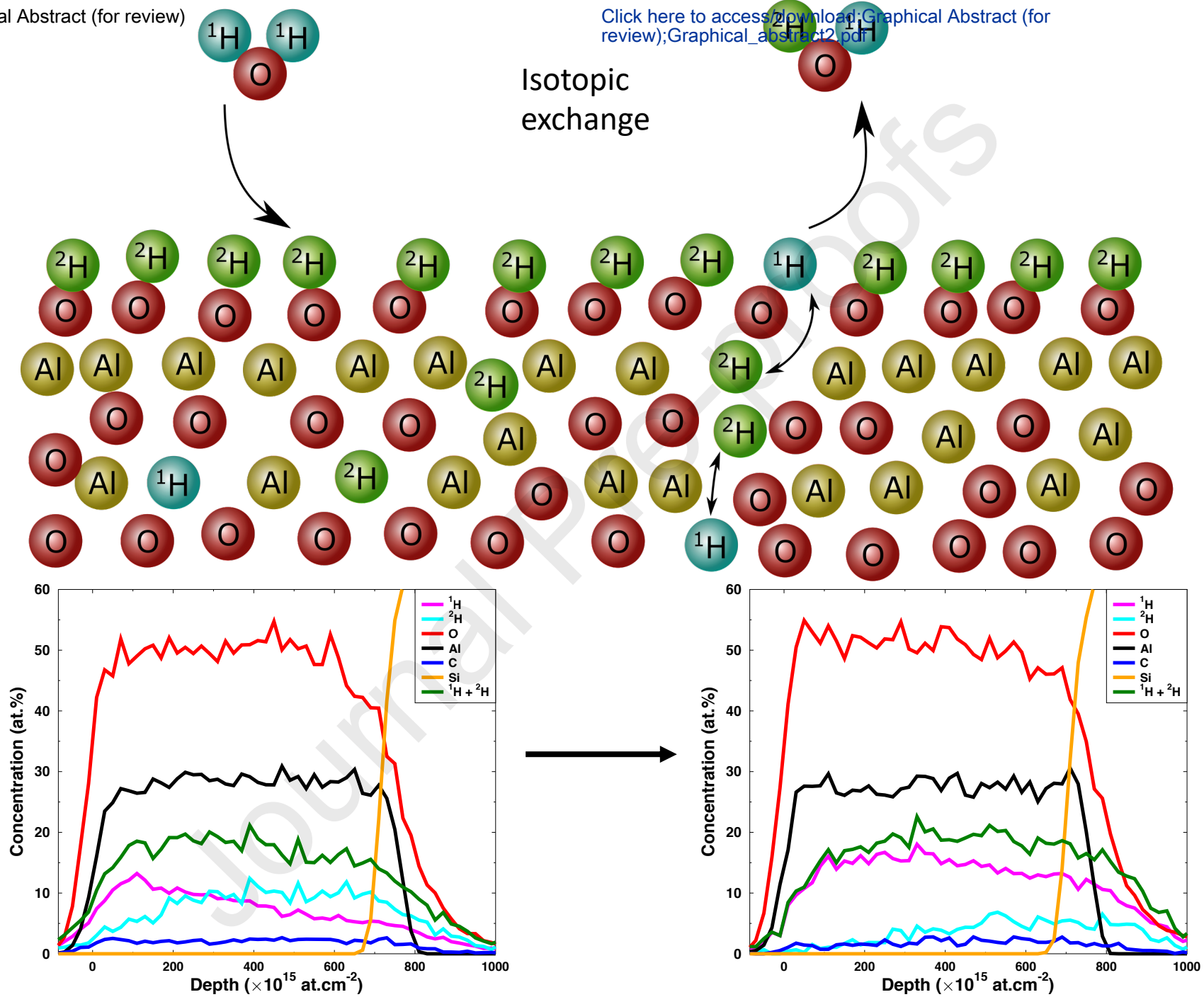
Highlights

- Concentration and source of impurity H was studied using isotopic labeling
- H and C impurities decrease with increasing deposition temperature and purge time
- Hydrogen isotopes can migrate in the film even at room temperature
- Migration occurs only if H concentration in the film is high enough

Graphical Abstract (for review)



Credit Author Statement

Sami Kinnunen: Investigating, Visualisation, Writing - original draft preparation. **Kai Arstila**: Investigating, Writing – Review & editing. **Timo Sajavaara**: Supervision, Writing – Review & editing