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RBS and NRA analysis for films with high growth rate prepared by atomic layer deposition

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Abstract

We present the design and operation of a specialized Atomic Layer Deposition (ALD) system, dedicated to stable isotopic tracing experiments of oxide film growth, using isotopically labelled water as the oxide reactant. A small chamber volume allows operation with only very small quantities of water vapor, minimising the consumption of the isotopically labelled water. The first results for growth of ZnO and TiO₂ using Diethylzinc (DEZ) and Tetrakis(dimethylamino)titanium (TDMAT) as the zinc and titanium precursors, and unlabelled water as reactant, are presented, to establish the growth conditions for stoichiometric ZnO and TiO₂ on silicon. Absolute film compositions and thickness are determined by RBS and NRA as a function of vapor pulse duration, number of ALD cycles and substrate temperature. Physical thickness is determined by ellipsometry. The first results obtained for growth of ZnO using water highly enriched in ¹⁸O are also presented.

Key words: Atomic Layer Deposition (ALD), Thin films, multilayer, RBS

1. Introduction

Atomic layer deposition (ALD) is a technique to prepare high quality thin films, with a controlled thickness and uniform composition through sequential self-terminating gas reactions [1, 2]. The ALD technique has been used to prepare water and oxygen barrier layers [3], conductive electronic films [4], transistor dielectric layer [5] and surface passivation layer [6] with applications in micro-electronics [7], solar batteries [8] and flexible electronics [9]. ALD also allows growth on high aspect ratio structures, allowing conformal coating of nanoparticles [10], and nanoporous [11] and nanostructured systems [12]. Due to great potential applications of ALD films, much attention has been paid to industrialization of the ALD technique. Yong-June Choi's team has developed an ALD machine for depositing ZnO and study its growth mechanism, the growth rate of ZnO films could reach to about 1.5 Å/cycles at 140°C [13]. David H. Levy designed a fast opening air atomic layer deposition system for preparing the films, which has a maximum growth rate for ZnO films of approximately 1.2 Å/cycle [14]. Seong Keun Kim who used the commercial ALD system (Ever-tek, Plus-100), prepared oxide films and obtained a maximum growth rate of almost 2 Å/cycle for ZnO [15]. Although the development of commercial and home-made ALD equipment allows growth of many kinds of thin films, the film growth rates remain relatively low compared to those obtained by the CVD process. So, there is still a lot of room for the further development and promotion of atomic layer deposition equipment.

In this paper, we introduce a novel ALD chamber combining a small volume, hot substrate/cool chamber and precursor cross-flow design. This design minimizes premature precursor decomposition and allows economic use of expensive isotopically enriched precursors for growth mechanism studies.

We chose first to grow ZnO and TiO₂ films because growth of these is well established, with numerous applications, and in addition, the high mass of the cation (compared to the very widely grown Al₂O₃) substantially simplifies RBS measurements. Films were grown from water and DEZ (ZnO films) or TDMAT (TiO₂ films) precursors. Absolute film elemental compositions were determined by RBS, and NRA, and film physical thickness was determined by ellipsometry. The effects of the number of ALD cycles, precursor pulse duration and substrate temperature were investigated. We also grew some films using water highly enriched in ¹⁸O.

2. Experiment

2.1. System description

The home-made ALD system consists of three parts: precursor, oxidant and carrier gas handling system, cross-flow design hot substrate/cold reaction chamber and a pumping system controlled by an in-house Labview control system (as shown in Fig. 1a). The DEZ and TDMAT precursor gases and the water vapour are controlled by fast valves. The flux of N₂ carrier gas is maintained by mass flow controller (MFC). A compact manifold system connects several precursor gas bottles to the single cross-flow gas inlet to the chamber. In our cross-flow design, gas enters the chamber through a nozzle nearly parallel to the sample surface, and is evacuated through the opposing face of the chamber by a dry pumping system. Compared with the traditional cross flow gas entrance our system has a small angle with sample surface. Such cross-flow design leads to more homogeneous film growth. The inlet nozzle has a wedge design, which has been shown to improve stability and homogeneity, and to increase deposition efficiency [16]. The sample holder is insulated from the chamber by a ceramic surround, and heated from the bottom by a resistive element. The sample surface temperature is inferred from the furnace thermocouple, via a careful series of calibration measurements. The passage of carrier gas and precursors in the chamber influences the target and chamber temperatures through convection and conduction. In order to limit transient temperature variations during the ALD sequence, we have developed a temperature control system based on a predictive temperature model. A typical series of precursor pressure pulses vs time includes water vapour pulse and purge time, and precursor pulse and purge time as shown on Fig. 1b.

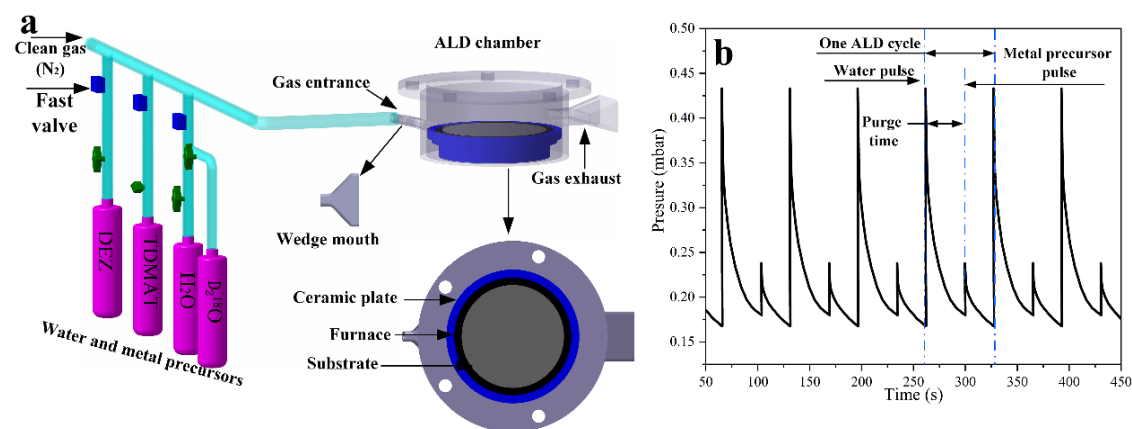


Fig. 1. a: Home-made ALD system included deposition chamber; b: the signal of pulse time of water and metal precursors

2.2. Experiment description

Si (100) wafers cleaned with acetone followed by absolute ethanol were used as the substrate. Diethylzinc (DEZ), Tetrakis (dimethylamino)titanium (TDMAT) and water were used as precursors. The pulse time of DEZ and TDMAT was fixed at 15 ms and 200 ms respectively, and the injection time of water was varied from 15ms to 100ms. A long N₂ purge time (30s) was applied in order to prevent precursors mixing during deposition. The sample surface temperature was varied from 100°C to 300°C and the number of ALD cycles was varied from 5 to 40 for growth of ZnO films and from 5 to 150 for growth of TiO₂ films. The detailed parameters for deposition ZnO and TiO₂ films are summarized in table 1. In this paper, we will present films grown using water of natural isotopic composition, and water highly enriched in deuterium and in ¹⁸O.

Table 1. Typical ALD deposition parameters for ZnO and TiO₂

Process parameters	Conditions
DEZ	Pulse 15ms + purge 30s
TDMAT	Pulse 200ms + purge 30s
H ₂ O/D ₂ ¹⁸ O	Pulse 15-100ms + purge 30s
ALD cycles	DEZ: 5-40 cycles; TDMAT:50-150 cycles
Temperature (°C)	100-300°C
Pressure (pa)	50-70pa

2.3. The characterization techniques

RBS and NRA were performed on the SAFIR platform of Sorbonne University, Paris. Backscattering Spectrometry (RBS) was used to determine the Zn and Ti area density, employed 20-100 nA ⁴He⁺ beams of 1.8-2.1 MeV, in a 1mm diameter beamspot, with particle detection at 165° scattering angle. The detector solid angle was calibrated with 3% uncertainty using a Bi-implanted reference sample [17, 18]. Nuclear Reaction Analysis (NRA) was used to measure the ¹⁶O areal densities via the ¹⁶O(d,p)¹⁷O nuclear reactions, with respect to a thermal SiO₂ film, with [¹⁶O]=624.8×10¹⁵ atoms/cm² as deduced from the film thickness and density determined by ellipsometry[19]. An 860 keV deuteron beam of 85 nA in a 2mm beamspot was used, and the protons produced by the nuclear reactions were detected at 150° in a 300mm² detector behind a 13 mylar foil which stopped the high flux of elastically scattered deuterons from saturating the detector. ¹⁸O was determined by the ¹⁸O(p,α)¹⁵N nuclear reaction with 85nA of 750 keV protons in a 2mm beamspot, and the alpha particles detected at 150° in a 300 mm² detector behind a 13 μm mylar film. The physical film thickness obtained from spectroscopic ellipsometry (SE) with a FS-1 Multi-

Wavelength Ellipsometer system in the wavelength range of 465-635 nm at an angle of incidence of 65°.

3. Results and discussion

3.1 The growth of ZnO

Fig.2 shows the growth per ALD cycle measured by ellipsometry as a function of the substrate surface temperature with a DEZ precursor pulse time of 15ms and H₂O pulse time of 100ms for each cycle. The resulting film thickness ranged from 16 to 60nm. The highest growth rate, of about 14 Å/cycle, occurs in a temperature window between 140 °C and 175°C. At substrate temperatures outside this range the growth rate falls. At lower substrate surface temperatures the DEZ precursors might not have sufficient energy to react with the -OH groups on the surface [15]. At temperatures above 175°C M. Rueter [20] has proposed that the lowered growth rate is due to surface thermal decomposition of the DEZ. In our system, although the chamber is not deliberately heated thermal radiation from the substrate still increases the temperature of the elements surrounding the substrate plate, including the chamber walls, where the DEZ may be decomposed into Zn and ethyl fragments, inhibiting growth on the substrate. The stable growth rate in the temperature window between 140 and 175°C suggests that self-limiting ALD growth of ZnO films has been obtained, as has been observed for very similar ALD windows in previous works [21-23].

The number of water molecules adsorbed on the surface is related to the pulse time, whilst substrate temperature has a strong influence on the formation of -OH groups formed from the adsorbed water molecules. We therefore investigated the influence of water pulse time on ALD growth within the ALD window. In Fig 3a, we show the number of Zn atoms (determined by RBS) as a function of number of cycles for water pulse times of 15, 50 and 100ms. In all cases film growth is achieved, and after about 10 cycles the growth rate increases as the water pulse time is increased. Clearly, for the shorter water pulse times full coverage of the surface by -OH groups is not achieved. During the first 10 or so cycles, the growth rate is limited by the surface group preparation, as is commonly observed [24, 25]. Here, the substrate surface is still very smooth as measured by AFM with value about R_q=0.38nm, whereas after the initial cycles the substrate surface can become rougher and facilitate adsorption of water molecules. In Fig 3b, the ratio of Zn to O atoms is plotted as a function of the number of ALD cycles for the 3 water pulse times. The films are all initially deficient in Zn for the first growth cycles, however the ratio of Zn to oxygen increases as water pulse time increases.

This indicates that when the surface is inadequately covered with -OH groups, the reaction of DEZ with the -OH groups is hindered, and it is possible that some of DEZ desorbs from the surface in regions where the -OH coverage is low. Previous study also illustrated that substrate-inhibited growth is caused by a lower number of reactive sites on the substrate than on the ALD-grown material [26, 27]. Since the depth resolution of NRA is unable to distinguish between ¹⁶O in the native oxide of the silicon substrate and that in the overlying ZnO films, we have systematically subtracted the amount of oxygen in the substrate, as measured on an untreated virgin substrate from the same silicon wafer, from the oxygen contents measured for the “substrate plus film” samples.

There remains, however, some uncertainty about the actual number of oxygen atoms in the substrate oxide layer after the first ALD cycles and it is not yet clear to what extent possible underestimation of the substrate oxide film thickness (after the initial ALD cycles) could be responsible for the observed low ZnO ratios for very thin ZnO layers obtained after the first 5 to 15 cycles.

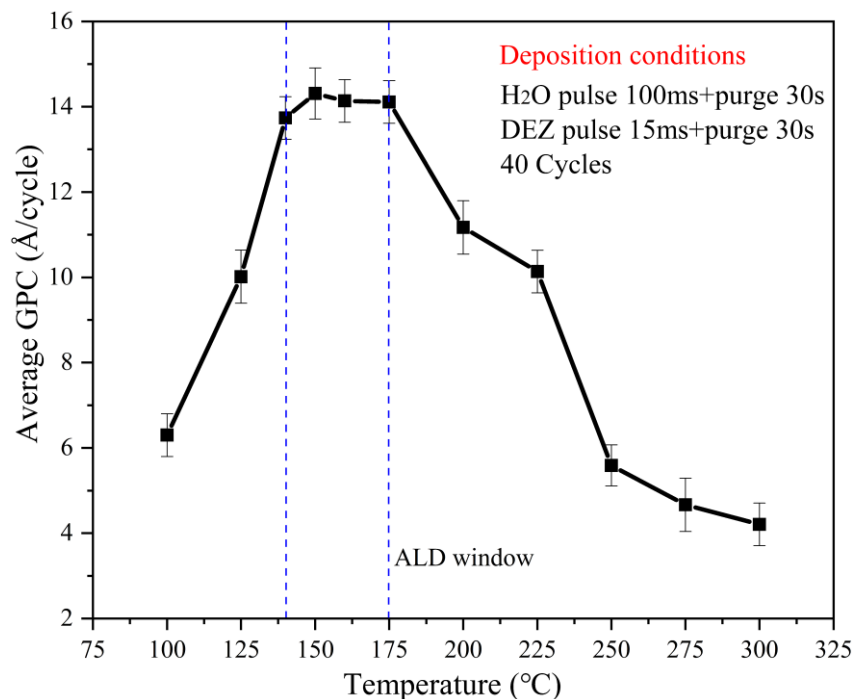


Fig.2. The variation in growth rate of ZnO films as a function of the substrate surface temperature. The number of ALD cycle was kept at 40 cycles.

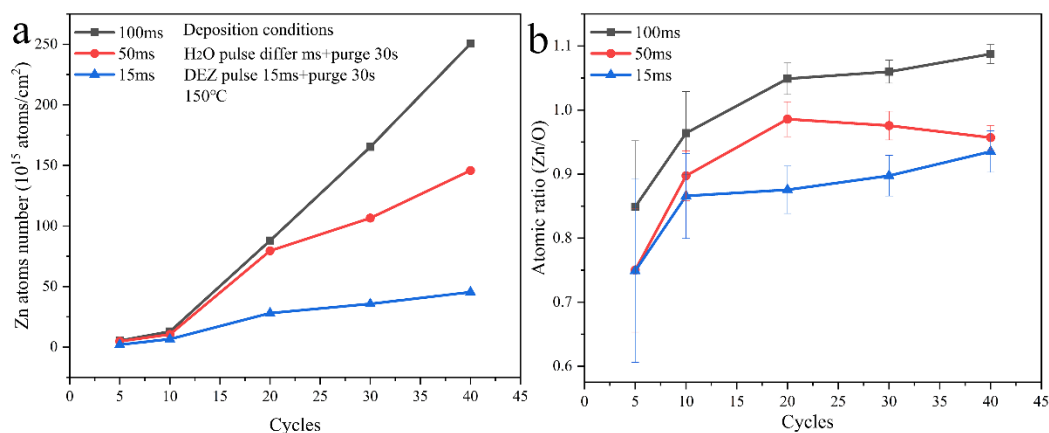


Fig.3. a: The variation in growth rate of ZnO films as a function of the ALD cycles at 150°C; b the variation in atomic ratio of Zn/O as a function of the ALD cycles at 150°C

3.2 The growth of TiO₂

Fig.4 shows the growth rate of TiO₂ as a function of the substrate surface temperature with a given TDMAT precursor time of 200 ms and H₂O precursor time of 100 ms. At low temperature, the film growth rate is much higher than at high temperature. It has been shown [28, 29] that TDMAT has an activation energy of just 16 kJ/mol (0.17eV) for adsorption in the low-temperature regime,

indicating a thermally activated adsorption surface process. In other words, numerous TDMAT molecules have an energy sufficient for adsorption to the low temperature surface which causes a high growth rate at the low temperature. The growth rate will decrease as the sample surface temperature is increased from 100°C to 250°C. This behavior is different from many models of ALD processes in the low temperature region. For this case, temperature programmed desorption (TPD) showed that the most of the TDMAT desorbed from the surface as the temperature was increased [30]. Hence, the growth rate of TiO₂ films will initially reduce with increasing surface temperature. We note that as the temperature is further increased, the growth rate of TiO₂ films increases. The increase in growth rate above 250°C is probably due to chemical vapor deposition (CVD) attributed to the gas phase decomposition of TDMAT. The team of Elam et al. also reported that the decomposition of TDMAT become more important for ALD deposition of TiO₂ at high temperature [31].

Based on the study of influence of substrate temperature on deposition, it was chosen to study the process at low temperature because the growth rate is very high - a clear advantage for commercial application. Hence, the temperature of 100°C was selected to study the effect of the water pulse duration, which was varied from 15ms to 100ms. In Fig. 5a we observe that for 15ms pulse time, the growth rate of TiO₂ films is clearly lower than that for 50ms and 100ms water pulses. The increase of film growth rate with water pulse duration strongly demonstrates that an adequate amount of water needs to be supplied during the ALD process. For the explanation of the increase of growth rate, although deposition of the water and -OH on rutile TiO₂ surface is temperature-independent [32], higher water exposure will likely lead to higher water and -OH coverage, providing more active sites for TDMAT reaction. We also observe, in Fig. 5b, that the Ti/O atomic ratio is highest for the samples grown with 100ms water pulses, further supporting that view that the shorter water pulse times didn't provide enough active sites for TDMAT reaction.

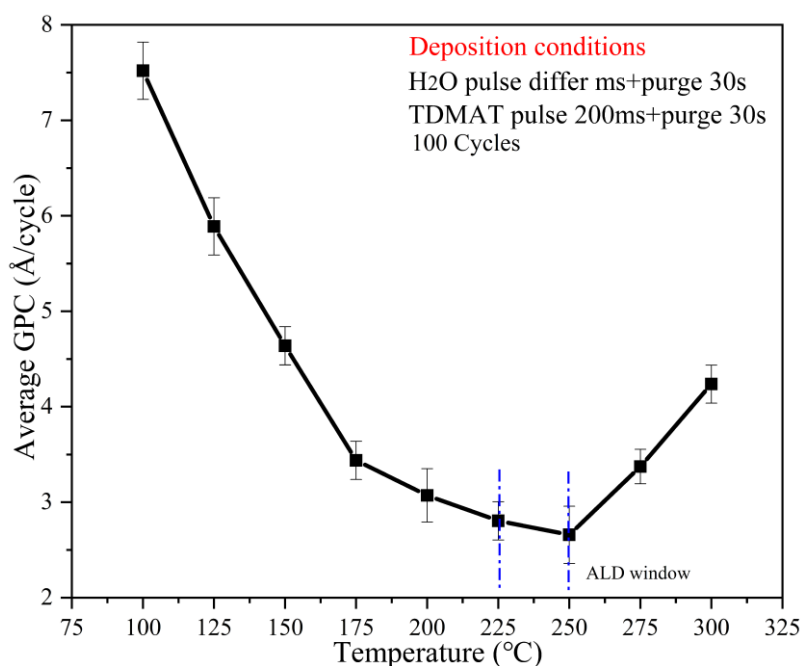


Fig.4. The variation in growth rate of TiO₂ films as a function of the substrate surface temperature. The number of ALD cycle was kept at 100 cycles.

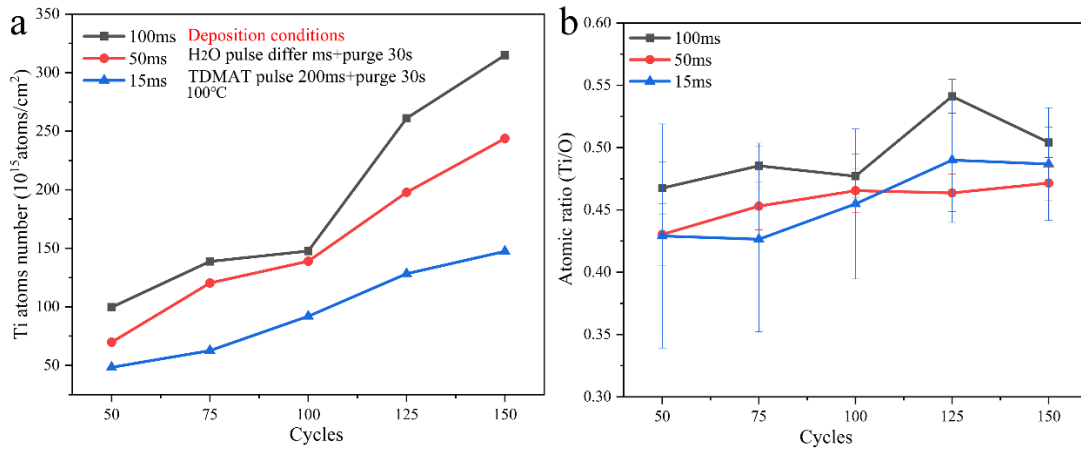


Fig.5. a: The variation in growth rate of TiO₂ films as a function of the ALD cycles at 100°C; b the variation in atomic ratio of Ti/O as a function of the ALD cycles at 100°C

3.3 Double layer and multilayer films

Based on the previous experiments, double layer films with 50 ALD cycles for ZnO and 100 ALD cycles for TiO₂ were prepared at the single temperature of 225°C, which is within the ALD window for TiO₂ and slightly above it for ZnO, in view of preparing multilayer films, for which using separate temperatures for each layer would require substantial deadtime for temperature equilibration between the growth of each layer. Films were prepared for ZnO-first and for TiO₂-first growth. Fig 6 shows the RBS spectra measured with 1.5MeV ⁴He incident ions, and the respective best SimNRA [33] fits, for the TiO₂-first (Fig 6a) and ZnO-first (Fig 6b) systems. We may note that the film thicknesses are not the same under the two different growth orders: the growth of ZnO on TiO₂ is accelerated compared with that of ZnO on the Si substrate, whilst the growth of TiO₂ on ZnO is retarded with respect to that of TiO₂ on the silicon substrate. To our knowledge this has not been reported previously, and we do not have an explanation for this observation, however further work studying the effect of the thickness of the TiO₂ layer on the acceleration of the ZnO growth, and the detailed growth kinetics (does the growth rate enhancement reduces as the ZnO film thickness increases?) should throw significant light on the underlying processes.

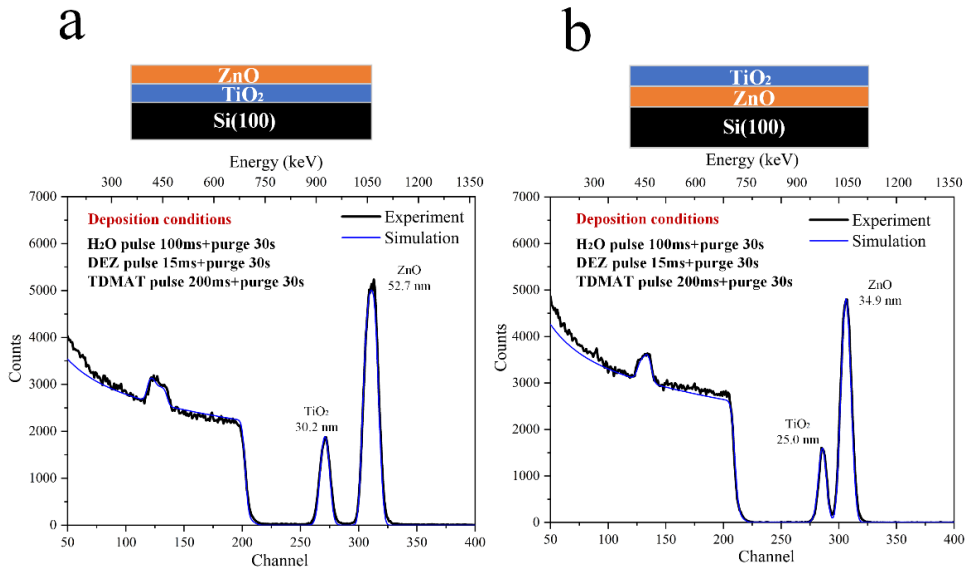


Fig.6. RBS spectrum and simulation by SimNRA for ZnO-TiO₂ double layer films. a: TiO₂-first; b: ZnO-first.

ZnO/TiO₂ multilayer films were deposited onto Si (100) substrates by repeating 80 TiO₂ ALD cycles and 30 ZnO ALD cycles at 225°C with the same precursor, water and purge times as for the bilayers described above. The RBS spectrum measured with 2.05 MeV ⁴He incident ions is shown in Fig. 7a. The Ti and Zn peaks from the 6 layers are well separated, indicating well-defined TiO₂ and ZnO layers, and the spectrum can be fitted well by SimNRA. The layer thicknesses are given in table 2 from top to bottom. The TiO₂ film thicknesses are quite uniform and in this case we do not observe the retarding of the TiO₂ growth rate on ZnO compared to that of TiO₂ on the substrate. We do note, though, that the growth rate of layer 5 (the first ZnO layer, on TiO₂) has been accelerated as was observed in the bilayer system. These observations indicate that there may remain some uncontrolled parameters, such as thermal inertia in the substrate holder or surrounding elements, or chemical memory effects in our growth system. Table 2 also presents the density of each layer, for the ZnO layer, the density is little lower than the ZnO bulk density with value 5.61 g/cm³, the density of TiO₂ is closed to the rutile density of TiO₂ (4.23 g/cm³).

Table 2. The thickness of each layer for multilayer film

Layer		10 ¹⁵ Atoms/cm ²	Thickness(nm)	Density (g/cm ³)
1	ZnO	252.0	30.7	5.5
2	TiO ₂	150.0	15.6	4.1
3	ZnO	245.0	30.4	5.4
4	TiO ₂	150.0	15.6	4.1
5	ZnO	312.0	37.7	5.5
6	TiO ₂	145.0	15.1	4.0
Si (100)				

Fig.7b shows the RBS spectrum of a ZnO film grown using water highly enriched in D²¹⁸O. We note here that the actual amount of water consumed for the growth of the film was too small to be observed, and we estimate that a few cm³ of enriched water will be sufficient for many hundreds of hours of operation.

The presence of both isotopes - ¹⁸O and ¹⁶O - is clear from the RBS spectrum but due to high background from the Si substrate and the resulting high uncertainties in estimating the areas under the oxygen signals, areal densities of ¹⁶O and ¹⁸O were measured precisely by NRA under conditions previously described [34]. Nevertheless, the RBS spectra do show that the two isotopes are present throughout the thickness of the films, and the simulated RBS spectrum using the quantities of ¹⁸O and ¹⁶O derived from NRA (given in the inset) are fully compatible with the measured RBS spectrum.

Although the water used was almost fully enriched in ¹⁸O, the film contains about 30% ¹⁶O. The total amount of ¹⁶O, of 100 × 10¹⁵atoms/cm², is far greater than that of the substrate native oxide and so must come almost entirely from the growth process, and probably from water adsorbed on the manifold, piping and chamber walls. This indicates that for future isotopic tracing studies of

growth mechanisms, special attention will need to be paid to outgassing the entire ALD system between growth sequences using different isotopically distinct water sources. We do note, that ALD films enriched even only to 70% in ^{18}O will be very useful for the study of annealing processes under standard conditions such as flowing air.

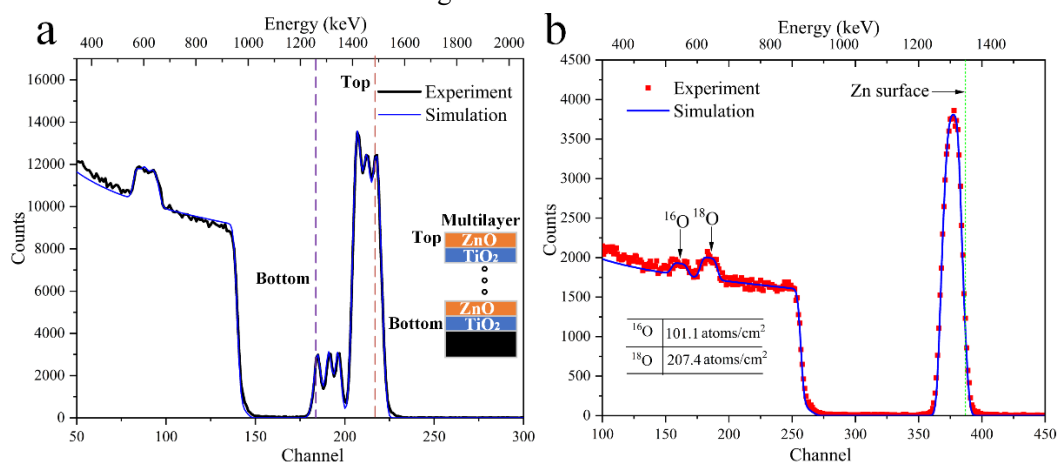


Fig.7. a: The RBS spectrum at 2.05MeV simulated by SimNRA. b: RBS spectrum and SimNRA simulation for ^{18}O enriched ZnO films.

Conclusions

We have successfully developed a home-made ALD system with high growth rates compared with established commercial systems. The system has been successfully demonstrated to grow stoichiometric ZnO and TiO₂ films, bilayers and multilayers. The small volume has enabled production of films highly enriched in ^{18}O , using only very small quantities of the expensive isotopically enriched water source.

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