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# Modification of the 306 Edwards sputtering system for the reproducible fabrication of sensitive thin films

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Modifications to the 306 Edwards sputtering system have been discussed for the production of sensitive thin films, specifically amorphous pyroelectric perovskite films. For technical reasons, it is not possible to produce high quality thin films using standard sputtering systems. Furthermore, additional problems arise with the reproducibility of the films. The authors found that in unmodified sputtering systems, a general problem is that independent adjusting of the pressure in the chamber and the gas flow during the sputtering is not possible. Additional problems were low accuracy of gas ratio measurements, and high temperature radiation during sputtering which made impossible keeping the temperature conditions during deposition. Modifications to a standard set-up have been proposed and its operation has been checked. As a test-case, $SrTiO_3$ thin film samples were fabricated. Their high quality confirmed validity of the modifications.

Keywords: *Edwards sputtering; thin film; vacuum system*

## 1. Introduction

The 306 Edwards sputtering system has been available for users for over 20 years. However some problems have been encountered with the production of sensitive thin film using this system. These popular sputtering systems were produced by Edwards until 2009 [1] and are still being used in many science laboratories for high quality thin film deposition [2, 3], including universities such as Massachusetts Institute of Technology and University of California at Berkeley. A detailed description of this sputtering system will be found at the official site of Berkeley Microfabrication Laboratory [4]. These systems are very good for the ordinary sputtering of metals and films, which is non-sensitive to sputtering conditions. But the production of films that are dependent on the stoichiometric ratio is very problematic. For example, the repro-

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*Corresponding author, e-mail: Victor.Shelukhin@weizmann.ac.il ducible preparation of amorphous thin films of $SrTiO_3$, $BaZrO_3$ and $BaTiO_3$ by this sputtering system [5, 6], namely thin films which do not crystallize during sputtering, remains a complicated technical problem. The reasons are the inadequacy of component systems (the pressure controller, gas injection and flow monitoring systems) and the fact that the gas injection and pumping systems cannot be controlled independently. Consequently, the pressure and gas flow ratio readings for this sputtering system have a 15% measurement error. Therefore it is almost impossible to obtain films of high quality, because that would entail much stricter production requirements: an exact $O_2$/Ar flow ratio should be maintained under a stable pressure and strong gas flow. It should be noted that uncontrolled thermal variations of the wafer during sputtering is a problem which also influences the sample quality. The sputtering modifications we describe here establish a procedure for the reproducible fabrication of high quality thin films, and this has been difficult to achieve before now. We demonstrate the effectiveness of our approach by producing pyroelectric films of $SrTiO_3$, but we believe our scheme can be used in more general cases.

## 2. Sputter modification

The Auto 306 rf and dc sputter coater with a turbomolecular pump consists of the following major components: Seiko turbo pump, short FL50 chamber, Poppet high vacuum isolation valve, rotary pump, liquid nitrogen trap, single button automatic vacuum control with Penning and two Pirani gauges, shutters; dc source advanced energy, rf source Dressler, two EPM75 magnetrons Edwards. The system allows the production of metal and dielectric films under $10^{-6}$ Torr base pressure.

The system auto 306 sputter has only three settings for the “Poppet” valve for the limitation of downstream: “Open”, “Close” and “Process”. The “Nupro” needle valves and Edwards “Pirani” vacuum gauges are used in the standard configuration to control the injection of gases into the sputtering system, for flow changes and pressure measurements. In order to obtain the requisite pressure in the chamber under “Process” mode, one has to change the gas flow. In other words there is no possibility of adjusting flow and pressure independently. As a result, with this sputtering system, there is a 15% measurement error for pressure and gas flow ratio readings. Therefore it is almost impossible to obtain films of high quality, because then an exact $O_2$/Ar flow ratio would have to be maintained, under a stable pressure and strong gas flow.

The following changes to the sputtering system (Fig. 1) were made:

1. Vacuum throttle valve (VAT series 61 butterfly control system) was added to enable selection, independently of the gas flow, of the pumping strength and the gas pressure in the chamber, in accordance with user requirements for experiments.

2. MKS baratrone type 622A and PM3 pressure controller were added to the system, for pressure measurements and for controlling the throttle valve.

3. The needle valves were changed to MKS type 247D four channel readout – for manual flow changes and type 1179A mass flow controller for precise gas injections.

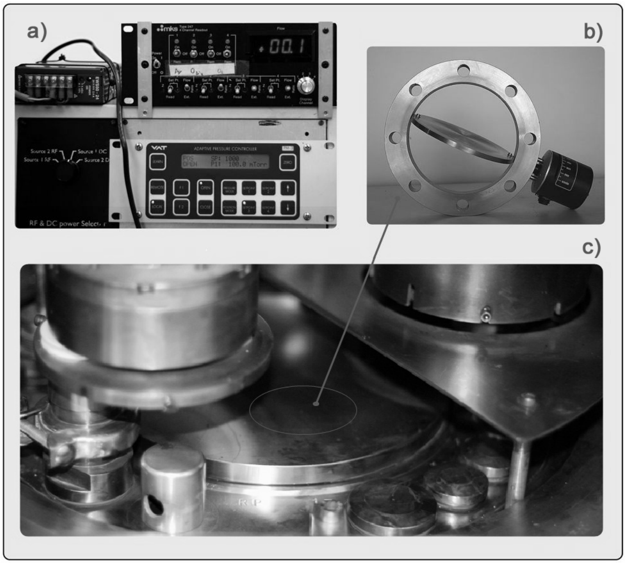

Fig. 1. Added instruments: MKS type 247D four channel readout and VAT PM3 pressure controller (a), butterfly VAT series 61 throttle valve (b), inside view of the sputtering system, new throttle valve is beneath a "Poppet" valve (in the ring) (c)

The introduced modifications allowed us to change the pressure in the chamber and the flow of each gas independently and, as a result, to obtain thea measurement accuracy of 0.1–0.2% for the flow ratio, and 0.5–1.0% for the pressure. We find that the temperature of the sample during the sputtering is very significant, because the temperature of the wafer critically influences the crystallization of the sputtered layer during the sputtering process. Therefore, in order to minimize the heating of the samples, it was necessary to construct a special holder, placed in the vacuum system and having reliable components, and which has good thermal contact with the chamber or can facilitate the cooling of samples in another way. In our case, to reduce heat build-up in the samples during the sputtering process, Si wafers were placed in a special, massive sample holder equipped with a heat sink. The temperature of the samples was directly measured on the wafer in the control experiment, using irreversible thermometers "SPIRIG". If the temperature of a sample during deposition was below 71 °C, amorphous layers of good quality were obtained, while if the temperature was higher than 143 °C, the films crystallized. If the temperature was between 71 °C and 143 °C, the samples were partially crystallized, depending on other parameters of experiments (thickness of SrTiO$_3$ layer, metals used for a bottom layer, etc).

## 3. Results and discussion

As a result of the modifications, reproducible, good quality films were obtained. More than 20 experiments were conducted, in each SrTiO$_3$ was sputtered onto Si substrate or Si/SiO$_2$ wafer covered with metal (Cr and W). Highly doped 2 inch Si wafers with the resistivity of 0.2–20 Ω·cm were used. Kurt J. Lesker targets were applied of the aforementioned materials (Cr or W), of 99.99% purity, for metal sputtering in an Ar atmosphere under the pressure of $1.2\times10^{-2}$ Torr and flow 2 standard cubic centimeters (sccm), in a dc mode, at 100 W power. The thicknesses of the metal layers were 150–200 nm. The sputtering of the SrTiO$_3$ films (using target – Semiconductor Materials, 99.9%, metal base) was done in an rf regime, without opening the chamber after metal deposition, in an Ar and O$_2$ atmosphere under $3\times10^{-2}$ Torr and 12 sccm flow of each gas, 100 mm distance between the target and Si wafer (or metal covered SiO$_2$/Si wafer). In the rf mode the power regime was 100–120 W and the thicknesses of the films were 65–120 nm. The base pressure in the chamber was $(1–2)\times 10^{-6}$ Torr. The temperature of the samples was up to 60 °C.

The gradient heating procedure (pulling through a temperature gradient) was done after sputtering in the manner described in the paper [5], for film transfer to quasi-amorphous state and followed pyroelectric measurements [7].

More than 80% of wafers were sputtered with 65–120 nm SrTiO$_3$ films were useful after top 2×2 mm$^2$ metal contacts evaporation and lift-off process, for making pyroelectric measurements, and they exhibited pyroelectric properties. All the samples used had good stoichiometric ratios. The ceramic composition was identified by X-ray photoelectron spectroscopy (XPS). The data was acquired with an Axis-HS, Kratos analytical spectrometer. Exemplary data for one of the examined samples is presented in Table 1.

Table 1. XPS data for SrTiO$_3$ film on Cr/SiO$_2$/Si

| State | Peak | Atomic concentration [%] | Stoichiometric ratio* |
|---|---|---|---|
| As deposit | Ti 2p | 14.94 | 1.0 |
| | Sr 3d | 15.31 | 1.0 |
| | O 1s | 50.72 | 3.3 |
| After 100 s sputtering | Ti 2p | 19.93 | 1.0 |
| | Sr 3d | 19.27 | 1.0 |
| | O 1s | 55.19 | 2.9 |
| After 160 s sputtering | Ti 2p | 22.03 | 1.1 |
| | Sr 3d | 19.60 | 1.0 |
| | O 1s | 54.95 | 2.8 |

*Stoichiometric ratio data is normalized to the Sr content, data corresponds to Sr:Ti:O with 1:1:3 stoichiometric ratio within the limit of the measurement method error (10%)

These SrTiO$_3$ samples are examples of sensitive thin films because only good stoichiometric, amorphous films exhibit pyroelectric properties after gradient temperature pulling [8, 9]. Wafers sputtered with SrTiO$_3$ were divided into two sets of samples, and each individual sample had dimensions of 6×40 mm$^2$; one set of samples was used for checking certain physical properties such as refractive indices, stress and composition measurements etc. The other set, consisting of more than 30 samples, was used for pyroelectric measurements: typical pyroelectric raw data from several of these samples is presented in Fig. 2. As can be seen from this figure, a time-dependent pyroelectric signal, generated in response to laser pulses used for sample heating, was recorded.

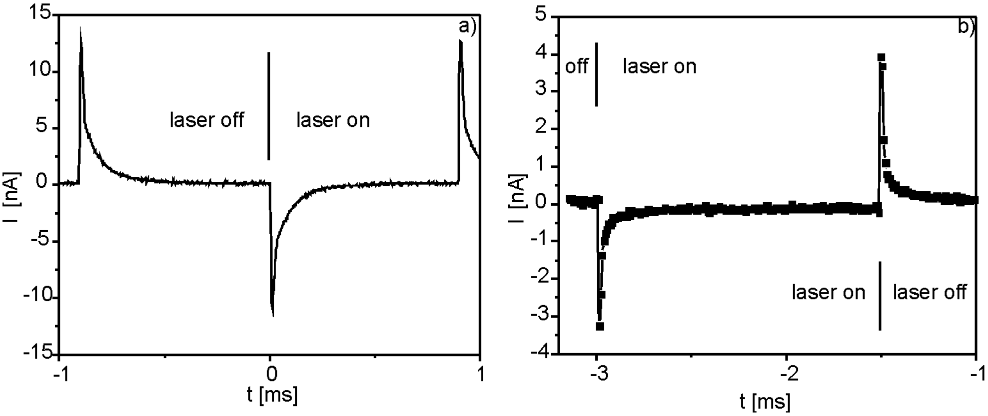

Fig. 2. Raw data from Tektronix TDS 7104 digital phosphor oscilloscope for several samples: a) Cr–$SrTiO_3$–Cr), b) W–$SrTiO_3$–W

Sr, Ti and O can form a variety of structures, perhaps $SrTiO_2$ [10], $Sr_2TiO_4$ [11], $SrTiO_{2.72}$ [12], $SrTiO_{3-x}$ [13, 14]. We assume that diversity of sputtering conditions (first pertinent of all – the oxygen content in the sputter chamber) leads to the formation of diversely different compounds. Furthermore, if conditions fluctuate during the sputtering process, this leads to formation of a nonstoichiometric film: XPS analysis confirms structural differences at different film depths in the film samples.

The XPS data for good samples is profiled by the data in Table 1. The surface contamination (mainly C, OH groups and water oxygen) was removed after 50–100 s of sputtering during XPS process, after then the stoichiometric ratio was measured, with the reservation that a tendency for Ti metallization is encountered.

Non-stable conditions and/or non-homogeneity of the process can all lead to defect formation, which provides crystallization centres. Failure to prevent high temperatures in the wafer also leads to crystallization of sputtered film, whereas samples maintained at low temperature do not crystallize during sputtering. It is possible that high temperature affected crystallization by itself or crystallization was a result of local extremely high temperature at some places on the substrate. But low temperature certainly prevents crystallization during the sputtering process.

Factors which are taken into account in the choice of a contact material are: quality of adhesion, temperature stability, unstressed growth during sputtering and stresses induced into a film during post-sputtering annealing (pulling samples through the hot zone). In order to find an appropriate metal for contact, five metals such as Au, Ag, Cr, W, and Mo were examined. Some of these metals have drawbacks: Ag does not allow elevated heating; Au has poor adhesion to $SrTiO_3$; when Mo was used as the bottom layer, no stress changes were observed after pulling through the temperature gradient (the reason for such behavior is unclear and it is now under investigation). Cr and W were found to be suitable candidates for a metal contact layer. Good $SrTiO_3$ adhesion on these metals allows the growth of homogeneous defect-free films.

The time dependent pyroelectric signal generated in response to the laser switching was recorded and compared with the theoretical predictions. As shown in Ref. [9], this pyroelectric signal must satisfy the following: $I^2(t) \sim 1/t$ ($I$ is the electric current, $t$ – time), in accordance with theory. In our experiments, the same pyro electric behavior was found for all samples. Samples with two identical metal contacts, top and bottom, were used for the elimination of contact potential differences.

## 4. Conclusion

Modifications to the standard 306 Edwards sputtering have been described, implemented and tested. It was shown that they lead to reproducible fabrication of films of high quality, quasi-amorphous perovskite pyroelectric thin films in this case, as confirmed by XPS data and pyroelectric measurements.

It should be stressed that not only are the modifications to the sputtering system itself essential, but also author’s recommendations regarding the preparation procedures for making the films, are indeed a critically important factor for achieving successful results. Important factors for film fabrication are: the temperature regime (less than 70 °C on the sample) as well as the gas ratio of the flow for two gases during sputtering.

The authors hope that their sputter modifications and recommendations will be used for the preparation of thin films from other materials, and for more general uses than the fabrication of quasi-amorphous pyroelectric films.

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