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# Contamination by slow diffusers in ion implantation processes: The examples of molybdenum and tungsten

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ABSTRACT

A procedure to measure molybdenum and tungsten contamination in implantation processes by DLTS (Deep Level Transient Spectroscopy) is defined and calibrated for the evaluation of molybdenum and tungsten contaminant dose. The obtained calibrations are used to study molybdenum contamination in $BF_2$ implantations and tungsten contamination by sputtering from a previously contaminated wafer holder.

In molybdenum-implanted samples, the molybdenum level located 0.3 eV above valence band is revealed only. In tungsten-implanted samples, two levels are revealed. One of these levels is the tungsten-related hole trap located 0.4 eV above valence band. The other level does not correspond to any tungsten-related level, however it is related to the presence of tungsten and to the sample preparation process. The SPV (Surface Photovoltage) measurement sensitivity to tungsten contamination was also tested, and it was found much lower than the DLTS sensitivity, due to the low tungsten diffusivity.

This procedure was used to evaluate contamination in implantation processes. In $BF_2$ implantations, in addition to molybdenum, tungsten contamination is found. Molybdenum and tungsten contamination is found in boron implantation too.

The tungsten contamination induced by implantation in a previously contaminated implanter was quantified, and the efficiency of arsenic implantation as a decontamination process was tested. Finally, it was shown that TXRF (Total reflection X-ray Fluorescence) is much less sensitive than DLTS for monitoring tungsten contamination.

## 1. Introduction

Metal contamination in ion implantation has been widely studied [1,2]. Schematically, two main contamination mechanisms have been identified in ion implantation, i.e. sputtering from parts close to the wafer during the implantation and mass interference, either with or without changes of the ion mass and charge between the ion extraction and the mass selection. Sputtering was shown to be responsible for iron contamination [3], which can be reduced by implantation through a thin screen layer and can be suppressed by a suitable design of the wafer holder [4]. Well-known examples of mass interference are molybdenum contamination in $BF_2$ implantation [5] or in indium implantation when fluorine is present in the ion source [6], or even in boron implantation [7].

To quantify metal contamination from ion implantation processes, it is necessary to take into account that contamination is frequently located inside the silicon matrix, so surface techniques such as Total Reflection X-ray Fluorescence (TXRF) can miss or underestimate the contaminant amount. In addition, in the case of contamination with slow diffusers such as molybdenum, a very small amount per unit area may result in a significant concentration in the near-surface silicon volume, so this sort of contamination can be difficult to catch by surface techniques and still be harmful for devices. For instance, molybdenum and tungsten contamination were found to be detrimental for imager sensor devices even in very low concentration [8]. In addition, these contaminants are frequently missed by techniques based on recombination lifetime measurements, because the region analyzed by these techniques is usually much deeper than the region involved in molybdenum and tungsten diffusion [9–11]. It was shown that the Deep Level Tungsten Spectroscopy (DLTS) is the best choice to detect contamination by slow diffusers [12].

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However, DLTS measurements give the contaminant concentration in the space charge region of a *p–n* junction or of a Schottky diode, i.e. in a limited region of the wafer. The formation of the required structures involves some process steps which may result in a loss of contaminant dose, so a calibration is needed to turn DLTS concentration data into contaminant amount per unit area.

In this paper, we set up a procedure to measure molybdenum and tungsten contamination in implantation processes by DLTS, and calibrated this procedure for the evaluation of molybdenum and tungsten contaminant dose. The obtained calibrations are used to study molybdenum contamination in $BF_2$ implantations and tungsten contamination by sputtering from a previously contaminated wafer holder.

## 2. Experimental details

### 2.1. Sample preparation

*P*-type, (100), 200 mm diameter, 725 μm thick 10 Ωcm resistivity Magnetic Czochralski (MCZ) wafers and *n*-type, 5 Ωcm resistivity CZ wafers were used in this study. Some samples were implanted with molybdenum or tungsten to calibrate DLTS measurements in terms of contaminant dose. The implantation conditions for molybdenum and tungsten are reported in Table 1.

The wafers for monitoring the contamination introduced by ion implantation were implanted with various dopant ions ($BF_2$, boron, arsenic) in the conditions reported in Table 2. The implantations were performed in an Axcelis NV-GSD200EE/80 High Current ion implanter. In $BF_2$ and boron implantations mass interference is expected to be the dominant contamination mechanism [5,7] and for this reason the impact of the material used for the ion source chamber (molybdenum or tungsten) was investigated.

Vice versa, arsenic in known to be responsible for a relevant contamination by sputtering [3,4], and therefore arsenic implantations ($10^{15}$ cm$^{-2}$, 60 keV) were used to monitor the contamination of the equipment after previous implantations of wafers with an exposed metal layer (tungsten). Some monitor wafers were implanted before contamination of the equipment, after contamination and after some decontamination cycles consisting of high dose arsenic implantations (1–2·$10^{16}$–cm$^{-2}$, 60 keV, 6.5·$10^{16}$ cm$^{-2}$, 75 keV) of dummy wafers, aimed at removing contamination by sputtering. After implantation, the metal surface concentration was measured by TXRF.

The calibration wafers and the wafers for contamination monitoring were treated according to the same process flow. The details of the flow used to prepare the calibration wafers and the samples to study the contamination from implantation in a contaminated implanter are reported in Table 3(a) and (b), respectively. After implantation, the wafers were thermally treated by A Rapid Thermal Process (RTP) at 1100 °C for 3 min in an inert environment. This thermal treatment had the purpose to allow the contaminant diffusion in silicon. Then, the wafers received a Reactive Ion Etching (RIE) of 1.2–1.4 μm silicon with the aim to remove the doped layer. The wafers implanted with molybdenum and tungsten were etched too, so the data obtained in these wafers can be directly compared to those of contamination monitor wafers. The samples for recombination lifetime measurements require no further treatment. To obtain Schottky diodes for DLTS measurements, the native oxide was etched off and 1000 Å titanium layer was deposited on the silicon surface, masked and etched.

**Table 1**
Implantation conditions of the calibration samples.

| Ion | Energy (keV) | Dose (cm$^{-2}$) |
|---|---|---|
| Mo | 8 | 1.5·$10^{10}$–$10^{11}$ |
| W | 8 | 1.5·$10^{10}$–1.5·$10^{11}$ |

**Table 2**
Implantation conditions of the samples prepared for contamination monitoring.

| Ion | Energy (keV) | Dose (cm$^{-2}$) | Ion source |
|---|---|---|---|
| $BF_2$ | 4 | 3·$10^{14}$–3·$10^{15}$ | Mo, W |
| B | 6 | 3·$10^{15}$ | Mo, W |
| As | 60 | $10^{15}$ | Mo |

Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) was used to investigate whether metal surface segregation may happen during the RTP thermal treatment. The samples for this investigation were implanted in the same conditions as in Table 1 and were annealed by the same RTP as the samples prepared for SPV and DLTS measurements. Of course, the samples prepared for ToF-SIMS analysis received no silicon etching. As-implanted and annealed samples were compared to assess metal surface segregation.

### 2.2. Experimental techniques

TXRF measurements were obtained by a RigakuTXRF300 instrument in direct mode, with the high energy beam at 0.05° angle and 500 s acquisition time for each point. The tool has a *W* filament working at 30 kV and 300 mA.

1 mm$^2$ area Schottky diodes were measured by DLTS. A Semilab DLS-83D instrument was used. In this instrument, lock-in integration is used for averaging capacitance transients, and temperature can be scanned in the range 30–300 K. Alternatively, constant temperature spectra can be obtained as a function of the frequency of excitation pulses in the range 0.5 Hz–2 kHz [13]. Both methods were used in this work.

The differential DLTS method was used. In this method, the Schottky diode (or the *p–n* junction) is reverse biased at a voltage $V_r$ and two filling pulses are applied: the first pulse $V_1$ is applied at the beginning of the lock-in integration period; and a second pulse $V_2$ is applied a half period later. In the lock-in integration, the difference $\Delta C$ is obtained between the integrals of the capacitance transients caused by the first pulse and by the second pulse. This method yields the trap concentration $N_t$ in the interval $[x_d(V_1), x_d(V_2)]$, where $x_d$ is the depletion region edge at a given reverse voltage.

In our measurements, samples were reverse biased at −5 V, and filling pulses with amplitudes of −0.5 V and −4.5 V were applied with a pulse width of 20 μs during each integration period. Under these conditions, a region ranging from about 0.8 μm to 2 μm was analyzed. The spectra shown in this paper were obtained with a 23 Hz filling pulse frequency. Schottky diodes were used for these measurements, so majority carrier traps could be revealed only.

SPV measurements are carried out by illuminating the sample with light of various wavelengths. Generated minority carriers are collected in the depletion region at the wafer surface and produce a variation in surface potential, which is recorded as a function of light wavelength. In the standard SPV technique [14], the diffusion length $L_{\text{diff}}$ (or the recombination lifetime $\tau$) is extracted from these data by assuming that sample thickness is much larger than diffusion length. This hypothesis often fails in present wafers, and the actual wafer thickness must be taken into account. An "enhanced SPV" [15] technique is available for this purpose. In this work, enhanced SPV was generally used.

Both standard and enhanced SPV are only sensitive to bulk recombination, so SPV cannot detect surface-segregated