Total sputter yield of LiF induced by hyperthermal ions measured by a quartz microbalance

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The total sputter yield of LiF induced by singly charged hyperthermal He+, Ne+ and Ar+ ions with a kinetic energy of 5–500 eV is presented. The measurements have been performed with a highly sensitive quartz crystal microbalance. Results of the total sputter yield for Au show excellent agreement with the literature. The results on LiF show a large and slowly decreasing total sputter yield at low energies. This fact is interpreted as evidence for electronic processes in the sputtering of LiF.

1. Introduction

In recent years, much attention has been paid to the secondary ion sputter yield [1–4] and relative sputter yields of alkali halides [5]. Nevertheless, no data for the total sputter yield were available, though only this one reveals the effectiveness of sputtering on insulators. One interesting question in the sputtering of insulators is the influence of the potential energy of the projectile on the ejection of target atoms. This should be visible at very low impact velocity, where all processes induced by ballistic sputtering are drastically reduced. In this paper we present first results of the total sputter yield on LiF induced by singly charged rare gas ions He+, Ne+ and Ar+ at very low impact energy. The experimental method which we used to determine the total sputter yield is a quartz crystal microbalance. The advantage of this method is the high accuracy of the quartz oscillation frequency, which is a direct measure of the mass removal during sputtering. Further, we measured the sputter yield of gold to confirm our results by comparison to the results of well established methods in the literature. For targets, we used a thin Au layer (100 nm) and a thin LiF layer on AT and SC cut quartz crystals.

Whereas quartz crystals are widely used for determination of the areal density and hence the thickness of deposited material [6,7], measurements of material removal were mainly done with different techniques, such as the conventional microbalance and RBS [8]. This is not astonishing, since the use of quartz crystals for sputter yield measurements encounters several problems. The rates of material removal and hence the frequency changes are rather low compared to most deposition applications, requiring high frequency stability of the crystal and oscillator circuit as well as high accuracy and resolution of the frequency measurement. Furthermore, much energy is deposited by the primary particles into the sputtered surface, causing problems of thermal drift. In many deposition applications, the energy deposition per incident atom is only a few eV (sublimation energy plus heat radiation from the evaporation source), while in our case the energy deposited per sputtered atom ranges up to a few hundred eV. Other problems may arise from the sensitivity of the resonance frequency to surface stress.

The problem of energy deposition by the ion beam is avoided using the quartz crystal as a collector for sputtered material, as practiced by Betz and Husinsky [9] in sputtering insulators or by Grischkowsky et al. [10] investigating the effect of oxygen on the sputtering of metastable ions and atoms of Ba.

McKeown [11] was the first, to perform direct sputtering on a quartz crystal microbalance. He presented total sputter yield data for a Au film evaporated on a plane parallel quartz crystal, induced by Ar+ primary ions (μA) for energies below 100 eV. Schou and Ellegard [12–14] investigated sputter yields of solid rare gases Ne, Ar and solid N2 deposited on a quartz crystal microbalance. They sputtered thin films with 0.8–3 kV electrons and determined the mass loss during irradiation. Another quartz crystal microbalance experimental setup for direct total sputter yield measurements was used by Brannon [15]. He measured the chemical etching of silicon using a standard AT-cut crystal operated in first order at a frequency of about 6 MHz. The number of etched silicon atoms removed from the surface was of the order of one monolayer.

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The present work describes further improvement of this method, whereby we are able to detect mass changes of below $10^{-3}$ monolayers of thin films evaporated on the temperature stabilized SC-cut quartz crystal. This high sensitivity allows the use of very low current densities $\sim 10 \text{nA/cm}^2$, even for hyperthermal kinetic energies (5-500 eV) of the primary ions. Although the total sputter yield at these energies can be as low as $10^{-2}$ particles/incident ion we obtain a sufficient frequency change to determine the yield during a period of about 10 min. The improvements required will be discussed in more detail in the next section.

2. Experimental

The experimental setup of the ion beam and the UHV equipment have been described before [16-19]. Singly and doubly charged hyperthermal ions are produced in a Duoplasmatron ion source. Mass separation is done by a Wien filter and neutral particles are avoided by a bend of $3^\circ$ in the beam line in front of an aperture. The beam is well defined spatially (FWHM 0.5 mm at 500 eV) and in energy (FWHM 2-3 eV at 500 eV). The beam is scanned over the target area to obtain a homogeneous current density. The kinetic energy of the primary ions is finally between 5 and 500 eV and the current density below 100 nA/cm$^2$. The residual pressure in the target chamber was in the low $10^{-10}$ mbar range.

The quartz crystals used as target for the determination of sputter yields were coated with evaporated gold electrodes on a thin chromium adhesion layer. For measurements on lithium fluoride, approximately 100 nm of LiF were evaporated onto the front electrode from a Mo boat, whereas the measurements on Au were performed by direct sputtering from the electrodes. Deposition of the electrodes and LiF was done in a separate high-vacuum coating system (10$^{-6}$ mbar) at approximately 150°C substrate temperature with deposition rates of the order of 1 nm/s.

To check the quality and stoichiometry of the LiF thin films, we have compared the secondary ion yields induced by singly and doubly charged He and Ar ions on thin LiF films [3] and LiF single crystals [4]. The results show the same relative ion yields for both samples.

In the UHV target chamber, the coated crystals were cleaned by heating to 400°C for several hours and sputtering (500 eV Ar$^+$) until the O$^-$ secondary ion signal was below 0.5% of the Li$^+$ and F$^-$ signal of LiF. Due to diffusion from the Cr adhesion layer, the gold film was slightly contaminated by chromium. The Cr concentration, estimated from Auger electron spectroscopy, was below 5 wt% on the sputtered surface.

We have used two types of plano-convex (6 MHz, 14 mm diam.) quartz crystals, which differ mainly in their crystallographic orientation: The AT-cut (YX1) $- 35.25^\circ$ (rotation symbol after ref. [20]) is the standard orientation used for deposition monitors, but it has the disadvantage of being sensitive to radial stress with a relative frequency change of $2.75 \times 10^{-11} \text{m}^2/\text{N}$ [21]. This means that the frequency is not only sensitive to stress caused by implanted primary ions, interstitials, etc., but also that it is sensitive to radial stress caused by temperature gradients in the crystal. The SC cut (YXwl) $+ 21.93^\circ, -33.93^\circ$ is insensitive to radial stress, but has a lower piezoelectric coupling factor than the AT-cut and needs special oscillator electronics to suppress an unwanted vibration mode, which has a frequency approximately 10% above the main resonance.

Both crystals are operated in the lowest thickness-shear mode (i.e. a standing transversal wave with the wave vector perpendicular to the crystal surface), which has extrema in the resonance frequency at approximately 80°C for AT- and around room temperature and at 160°C for SC-cut crystals. To avoid first-order thermal effects, the crystal holder is resistively heated to this temperature. Since the AT-cut crystals exhibit an additional temperature sensitivity due to thermal stress, the ion beam was scanned over most ($10 \times 10 \text{mm}^2$) of the front surface of the crystal to reduce uneven heating, which would cause frequency jumps when the beam is switched on and off. On the SC-cut, it is sufficient to have constant ion current density in the “active” (vibrating) area of the crystal: therefore, the beam was scanned over an area of $5 \times 5 \text{mm}^2$ only. This allows higher current densities than with the AT-cut.

Possible slow drift of the frequency is eliminated by analyzing several periods with the beam switched on and off. To get the slope of the frequency change, straight lines were fitted to the measured data with the condition that they must have intersection points at the time the beam is switched on or off. Finally the differences of the on and off periods were statistically evaluated.

The electronics consist of a home-built gain-controlled oscillator circuit and a HP 5372A frequency analyzer with ovenized crystal time base. The whole system currently reaches a frequency noise level of approximately 10 mHz (rms) with AT- and 1 mHz (rms) with SC-cut crystals.

Since the deposited film is very thin compared to the thickness of the quartz crystal, it is sufficient to use the simple equation [6,7]

$$\frac{\rho \Delta l}{\rho_0 l_0} = -\frac{\Delta f}{f}$$  \hspace{1cm} (1)

for the determination of the mass loss from the relative

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change of frequency, $\Delta f/f$. Here, $\rho_F \Delta l$ denotes the change of mass per unit area and $\rho_O$ and $l_Q$ are the density and thickness of the quartz crystal.

3. Results and discussion

To verify the performance of the measurement setup, we have performed measurements of the sputter yield of Au induced by the primary rare gas ions He$^+$, Ar$^+$ and Ar$^{2+}$ for the kinetic energy range between 5 and 500 eV, which is already well known from the literature.

To determine the total sputter yield as a function of the kinetic energy, one has to consider two important facts which strongly influence the result. The first point is the measurement of the primary ion current. He, Ne and Ar induce secondary electrons with an efficiency of approximately 0.16, 0.20 and 0.03 at 500 eV [22,23]. Although this efficiency is rather independent of the primary ion energy, we used a Faraday cup to reduce the influence of secondary electrons on the total sputter yield. The second point is the energy dependent influence of primary ion deposition in the first monolayers, which influences the frequency change directly in the opposite direction of the sputtering effect at low ion doses before steady state conditions are reached.

It is therefore necessary to introduce a correction in the total sputter yield,

$$Y_{\text{corrected}} = Y_{\text{quartz}} + (1 - R) \frac{m_{\text{pr}}}{m_{\text{target}}},$$

where $Y$ is the total sputter yield, $R$ is the fraction of reflected and resputtered implanted primary ions and $m_{\text{pr}}$, $m_{\text{target}}$ are the masses of the projectile and target atoms, respectively. When the total sputter yield is low, the implanted ions become a dominating factor in measuring the total sputter yield. According to Ito et al. [24] and Biersack and Eckstein [25], we estimated a backscattering coefficient $R$ of 60% for 50 eV Ar$^+$ ions on Au. This gives a correction to the sputter yield of 0.08 at 50 eV kinetic energy. At high energies, the backscattering correction is below the accuracy limit of the measurements. For LiF we have proved at 100 eV Ne$^+$ bombardment that the measurements have been performed under steady state conditions. After a Ne$^+$ ion dose of $1 \times 10^{16}$ ions/cm$^2$, which corresponds to the removal of two monolayers, we observed no significant change in the sputtering rate (within the accuracy limit of 10%). Therefore the correction of the implanted ions must be much less than the upper limit of 0.7 calculated by Eq. (2).

Fig. 1 gives evidence for the high sensitivity of the quartz crystal microbalance and the good agreement of our measurements with theoretical and experimental data in the literature. For He$^+$ our data point at 500 eV kinetic energy is in good accord with the theoretical calculations of Eckstein [8] and within the experimental uncertainty of his data. The sputter yield data of Ar$^+$ are in good agreement with the experimental results of Laegreid and Wehner [26] and also with the theoretical values of Bodhansky down to a kinetic energy of 100 eV. In the energy region below 100 eV, the theoretical and experimental data differ by an order of magnitude. As mentioned above, a correction of our low energy results due to implanted ions is needed; with this correction, the sputter yield agrees quite well with the calculated data of ref. [8].

As expected, no significant difference in the measured sputter yield between singly and doubly charged projectiles was seen. Neutralization of the incoming ion by an electronic transition of an electron from the valence band to a free state of the impinging ion has no influence on the desorption process as in insulators [3,4,18,19], due to the short relaxation time of the electronic system in a metal.

Another way to test the accuracy of the method was the variation of the current density. The total sputter yield was constant over at least one order of magnitude for Au and LiF within the experimental deviations.

In the case of LiF we present the first experimental data for the total sputter yield induced by He$^+$, Ne$^+$ and Ar$^+$ ions, see Fig. 2. First we will discuss the results of Ar sputtering at room temperature and 160°C. Postawa and Metoudian [5] pointed out that the relative Na$^+$ yield induced by Ar$^+$ ions at 5 keV on NaCl increases with temperature. The Na$^+$ signal rises from room temperature by about a factor of 2 until it saturates at 80°C. Wurz and Sarntheim published ESD measurements of Li$^+$ on LiF, which show that in this system, saturation is reached above 150°C. This depen-
The yield of LiF is surprisingly high compared to that of metals, even accounting for an enhancement of the total sputter yield due to the 45° angle of incidence. Furthermore, it should be noted that $Y = 1$ refers to one sputtered LiF molecule per incident ion, i.e., the sputtering of two atoms per ion. In the whole energy range investigated, the yield decreases by about a factor of 2 for He$^+$ and 10 for Ar$^+$ primary ions. This is much less than for pure elements with a similar mass, such as Si, Al and Be, which show a yield decreasing by over three orders of magnitude in this energy range [8]. Even at an energy near 20 eV, the total sputter yield for LiF is $\sim 0.6$ for Ar$^+$ and therefore about two orders of magnitude higher than for Al or Si [8].

The results of sputtering with Ne$^+$ show a higher yield than those with Ar$^+$. This may be explained by the improved energy transfer from the Ne particles to the target particles, because of the better mass match. The total sputter yield induced by He$^+$ is slightly lower than that of Ar$^+$ at high energies, probably due to the low mass of He. This behaviour of the different gases has also been observed in measurements of sputtered Li$^+$ and F$^-$ ions [3,4]. At low energies, the He data show a nearly constant yield, different from Ar. However, we should remember that the correction for implanted ions is very low for He due to its low mass, whereas the data shown for Ar may be too low as already mentioned.

The high yields at energies below 100 eV strongly point to a mechanism different from kinetic sputtering. We know that the potential energy (i.e., ionization energy) of the projectiles can play an important role in the creation of secondary ions [3,4]. From this we conclude that there is also an influence of the potential energy on the total sputter yield, which is an electronic effect in sputtering. However, the yields of the secondary Li$^+$ and F$^-$ ions increase by four orders of magnitude in the energy range between 5 and 500 eV [3,4], which is not reflected in the total sputter yield. The explanation for this behaviour can be found in the neutralization of outgoing secondary ions which is much more effective at low energy.

In summary, we have presented measurements for the total sputter yield of Au and LiF measured with a highly sensitive quartz crystal microbalance. The results on Au show excellent agreement with data from the literature. The sputter yield of LiF decreases much more slowly than for metals. Therefore, the sputtering process of LiF cannot be explained by kinetic sputtering alone, but must be significantly influenced by electronic effects. Further investigations of the influence of the potential energy of the primary ion are required to gain further insight into these processes.

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