

Introduction

Glow discharge optical emission spectroscopy (GD-OES) is routinely used for the thick film analysis of solid samples, like steels or coatings, for quality control and technology developments. Electrically conductive and nonconductive layers gain permanently in importance. Examples for such films are hard coatings for surface protection, layers for the improvement of tribological properties or diffusion impeding layers in electronic devices and many other fields of application. Due to the rapid development in the nanotechnologies the layer thickness is often reduced to a few nanometers [1]. Our aim is to be able to measure thin layers with thicknesses less than 100 nm by GD-OES. All experiments were performed with the Spectruma GDA 750 in DC-Mode on a silicon wafer as model sample.

Problem

Because of the venting of the glow source before each measurement and the required short evacuation times using a pre-vacuum pump only, contaminations of films of water and hydrocarbons cannot be prevented. Increased surface temperatures due to heat transfer from the plasma activates the desorption of water and hydrocarbons during each analysis. These desorbed molecules are then pumped out and cause a delay of the adjustment of equilibrium in the plasma. This effect becomes more disturbing, the thinner the layers under examination are.

Origin of the contaminations

The contaminations give increased signals of hydrogen, carbon, nitrogen and oxygen. Three different ways how these elements can come into the plasma region are thinkable: from the analyzing gas (impurities, leakages), from the inner surfaces of the source and the sample itself. All following diagrams show exemplarily only the hydrogen signal to represent the contaminations. The effect of the sample cleaning procedures is given in Fig. 1. The contrast to the low signal of a measurement without venting demonstrates, that there must be an other origin of contamination in the source, e.g. the inner surface of the anode (see Fig. 2).

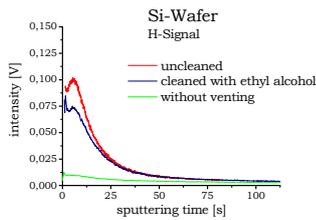


Fig. 1 Effect of sample cleaning: uncleaned – cleaned with ethyl alcohol measurement without venting, the difference must be caused by contaminations in the source

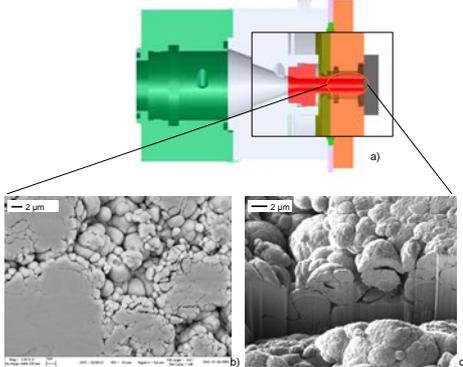


Fig. 2 Remained deposited sample material on inner surface of the anode
 a) Section cut of the glow discharge source – extended representation of the anode (red)
 b) SEM-topview of the only partially removed growing structures
 c) FIB cut showing the cauliflower-like structure inside these structures

Strategy

At the moment it is impossible to avoid that the source is vented during the sample change. Any transfer chamber would increase the total analysis time and make the sample change more difficult. Because the contaminations coming from the ambient atmosphere cannot be prevented, their elimination before the analysis will be of utter most importance. Not necessary to say that initially the vacuum system has to be optimized (detection of leakages and use of sealing material with low outgassing and/or permeability). Two main approaches can be taken into consideration. Firstly constructional improvements can influence the amount of gaseous elements in the plasma, by the change of the source geometry to lower flow resistance or the use of source materials with lower gas adsorption rate [2]. On the other hand the desorption can also be stimulated before analysis. The desorption rate is inversely proportional to the evacuation pressure. A combination of a pre-vacuum pump and a turbo molecular pump (TMP) can accomplish this lower pressure (see Fig. 3). Other thinkable treatments are different pump regimes, varying the times for evacuating and flushing; evacuating cycles. The desorption rate must also increase, when the inner surfaces of the source and the sample are heated by a gas heating or by an installation of additional heat sources in the chamber [3]. It is eminent that additional procedures or constructional changes don't increase the short analysis times and affect the easy operability.

Findings/Results

Additional to the pre-vacuum pump (Varian TriScroll 300, pumping speed: 210 l/min) a turbo molecular pump (Varian V70LP, pumping speed (N₂): 46 l/s) in a bypass configuration was installed (Fig. 3).

Within the first 3 - 10 s of the evacuation time at a pressure of ~ 0,1 hPa the turbo molecular pump is automatically switched on in the pumping line and after ~250 s we obtain one and after ~1500 s two orders of magnitude lower pressure (see Fig. 4). As expected, this leads to a reduction of the contaminations (represented by the hydrogen signal in Fig. 5) due to increased desorption rate during the evacuation process at lower pressure.

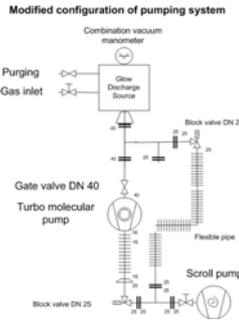


Fig. 3 Pumping system with scroll and turbo molecular pump

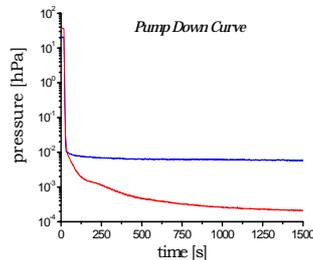


Fig. 4 Characteristically pump down curve of the source with and without turbo molecular pump

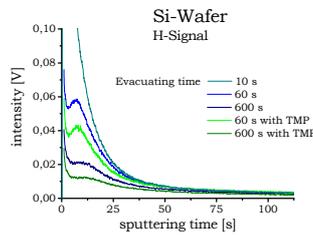


Fig. 5 Dependence of the hydrogen line intensity on pumping time and stimulated desorption by use of an additional turbo molecular pump

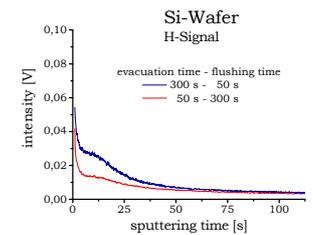


Fig. 6 Cleaning effect of evacuation and flushing time

After evacuation of the source a flushing procedure is effected. The flushing pressure must be in the range of the analyzing pressure (2-8 hPa) to be able to ignite the glow discharge and this takes normally some seconds only. Longer flushing times can also reduce the contamination in the discharge, even to a lower degree than longer evacuation times as can be seen in Fig. 6. The higher cleaning effect is assumedly due to higher gas flow. The source is polluted during venting while every sample change (see also Fig. 1). Fig. 7 shows that increased flow rate during venting – outflow of argon gas with little over pressure against atmospheric pressure – decreases the inflow of contamination when the source is open to atmosphere.

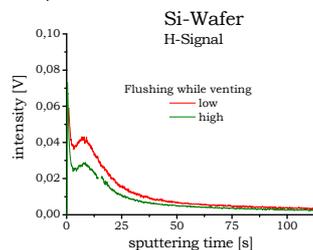


Fig. 7 Increasing the flushing during the sample change reduce the inflow of contaminations represented by the hydrogen line intensity.

The stimulated desorption of adsorb particles on surfaces is a known process to clean ultra high vacuum chambers in practice. There exist some approaches to irradiate or bombard the surface by particles or photons [3] to transfer energy to the adsorbed particles. This was also applied by a halogen bulb lamp (20 W) inside the source. Even if we measured surface temperature increases to more than 150 °C we could not recognize any big effect in the reduction of the hydrogen signal. It is imaginable that a repeated evacuation (stimulated desorption) and flushing (removal of molecules) could be reduced by an interactive process the adsorbed molecules from the inner surfaces. Two measurement was executed to test this dependence. One measurement with 10 cycles of evacuating and flushing and the other without (normal way) but with the same complete time (black and blue line in Fig. 8). No difference in the hydrogen signal could be detected. The result is probably dominated by the long flushing time.

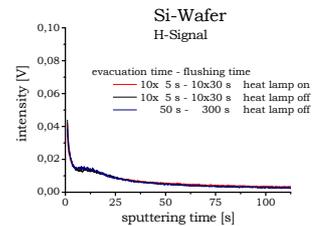


Fig. 8 No dependence of the hydrogen signal on pump cycles and heating the gas by a lamp

Application

A typical application, where GD-OES is an excellent method for quality control, is the depth profile analysis of deposited hard coatings. Fig. 9 shows for example the analysis of a titanium nitride layer. The light elements (H, C, O) disturb the stabilization of the Ti and N signals for the first 40 s (see Fig. 9a). Hence, it is impossible to evaluate the layer until a depth of approximately 300 nm. The use of some presented improvements (additional turbo pump, longer pumping and flushing time) reduces definitely the amount of H, C, O by a factor of 10. As a result the equilibrium in the plasma is faster obtain. The investigation of the upper hundreds of nanometer now succeeds much better, even if there is still a observable disturbing effect.

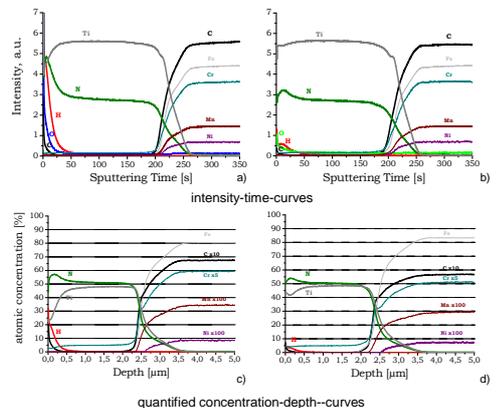


Fig. 9 DC-GD-OES measurement of a TiN-Coating on a steel substrate (thickness: 2.4 µm) with different measurement parameters
 a) c) evacuation time: 30 s, flushing time: 5 s, no turbo pump
 b) d) evacuation time: 300 s, flushing time: 300 s, turbo pump used for evacuating

Conclusion

Different procedures for the reduction of contaminations of source and sample were applied. A cleaned silicon wafer was used as a model sample to show the results. Alongside the installation of an additional turbo molecular pump the influence of some measurements parameter like evacuation and flushing time, cycles of evacuation and flushing were investigated. Also the flushing during the sample change influence the amount of gaseous elements observed during the next measurement. The use of a heat lamp inside the source for stimulating the desorption had no big impact, especially when long flushing times were applied. It was shown that longer flushing time reduces more the disturbing elements than longer pumping times. The rise in evacuating and flushing times prolongs the total time of analysis, which however is still considerably less than comparable methods as AES, XPS, SIMS require. Applying the results of the investigations for optimized measurement parameters to a technical sample helps to interpret the signals from the surface near region.

Literature

[1] Angeli J., J. Anal. At. Spectrom. 2003, 18, 670
 [2] Sumitsui, M., J. Vac. Sci. Technol. A, 1987, 5, 37
 [3] Edelmann Chr., Vakuumphysik, 1998