Plasma cleaning of multilayer coatings from carbon and tin contaminations

V.V.Ivanov*, A.S. Kovalev, D.V. Lopaev, T.V. Rakhimova, A.N. Vasilieva, O.V. Braginsky

** Institute of Spectroscopy RAN, 142190 Troitsk, Moscow region, Russia,* VladimirIvanov@isan.troitsk.ru

Skobeltsyn Institute of Nuclear Physics, Moscow State University, Russia, lopaev@dnph.phys.msu.su

Motivation

ML mirrors are supposed to be ones of the main elements for collecting and manipulating the EUV emission. In the open equipment the ML mirrors will undergo to the contamination. For Sn-based EUV source C and Sn are most probable debris that could contaminate ML surface. Thus it is of importance to develop methods of ML surface cleaning from the debris (C,Sn) in order to recover reflectivity of ML mirrors.

The object for investigation

MSU team used two models of "duty" ML mirrors which need to be cleaned. It is 100 mm silicon wafers with ML (Mo:Si) mirror on one side.

- One ML mirror was covered by tin of the thickness ~13.6±0.3 nm.
- Other ML mirror was covered by carbon of the thickness ~12±1 nm.
- Both wafers are broken in many small samples which then are undergone to the treatment and investigation.

Sn ML samples were analyzed by the dual-wavelength X-ray reflectometry and refractometry

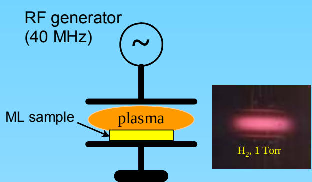
Measurements were carried out on X-ray reflectometer ***X-Ray MiniLab*** of "Unisantis SA" providing simultaneous measurements at two and more spectral wavelengths. In this investigation two lines Cu K_α (λ = 0.154 нм) and Cu K_β (λ = 0.139 nm) were used.

Results of X-ray reflectometry and refractometry

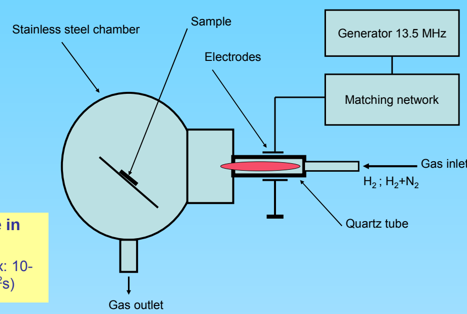
- Surface roughness of ML mirror – 0.3±0.1 nm.
- Period thickness of Mo:Si ML structure - 6.95±0.01 nm (Cu K_α - 6.94 nm, Cu K_β - 6.96 nm).
- The observed thickness of Mo:Si ML structure - 114 nm.
- Density of top Sn layer - ~90% from volume density of white tin.

Experimental setup

- **ML samples were cleaned by plasma etching. There were used two approaches.**
- **The first one is etching directly in H_2 (H_2+N_2) plasma, i.e. radical (H and N atom) etching assisted by ion bombardment.**
- **The second one is purely radical etching in the far afterglow of discharge, i.e. plasma is used as a source of radicals (H and N atoms).**



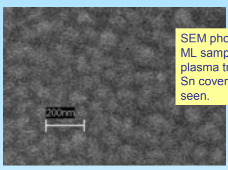
Experimental set up for ML cleaning in the CCP discharge in He, H_2 and mixture H_2/N_2.
Pressure: 1-5 Torr. Power density: 0.1-2 W/cm². Ion energy and flux: 10-50 eV and 10^{14}-10^{16} ion/(cm²s). H atom flux: 10^{16}-10^{19} atom/(cm²s)



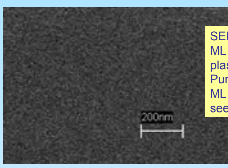
Experimental set up for ML cleaning in the rf discharge afterglow.
Pressure: 0.1-1 Torr.
Gases: H_2 and H_2:N_2=1:1.
RF power: 10-100 W.
Distance between center of plasma and sample ~20cm.

Cleaning of Mo:Si samples from Sn (results)

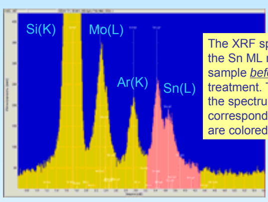
- **Analysis of Sn ML samples *before* and *after* the plasma treatment was carried out by using SEM and XRF technique.**



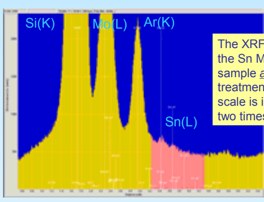
SEM photo of Sn ML sample *before* plasma treatment. Sn covering is well seen.



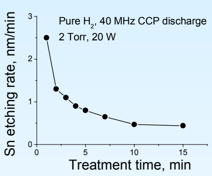
SEM photo of Sn ML sample *after* plasma treatment. Pure surface of the ML sample is well seen.



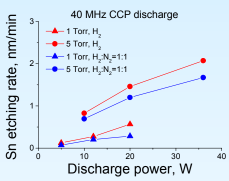
The XRF spectrum of the Sn ML mirror sample *before* plasma treatment. The part of the spectrum corresponding to Sn are colored by rose.



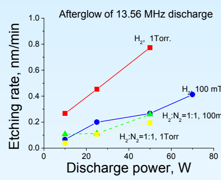
The XRF spectrum of the Sn ML mirror sample *after* plasma treatment. The Y-scale is increased in two times.



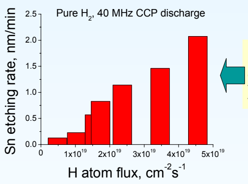
Etching rate of Sn layer in 40 MHz CCP discharge as function of treatment time.



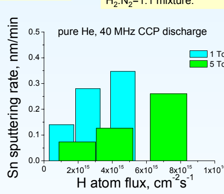
Etching rate of Sn layer in 40 MHz CCP discharge in pure H_2 and H_2:N_2=1:1 mixture.



Etching rate of Sn layer in the afterglow of 13.56 MHz discharge in pure H_2 and H_2:N_2=1:1 mixture.



Etching rate of Sn layer in 40 MHz CCP discharge in H_2 as function of H atom flux to the surface.



Sputtering rate of Sn layer in 40 MHz CCP discharge in He as function of He⁺ ion flux to the surface.

- In pure hydrogen etching by radicals (H atoms) predominates over ion sputtering although quite possibly the ion bombardment stimulates Sn etching. The probability to remove one Sn atom from the surface on one H atom incident to the surface can be estimated from the histogram slop in the first figure as ~(2±2)·10^{-9}.
- The sputtering rate of Sn by ions obviously depends on both mass and energy of ions. For He+ ions the probability to remove one Sn atom from the surface on one H atom incident to the surface can be estimated as (2÷8) ·10^{-6}

Summary

- Etching rates of Sn up to 1-2 nm/min in 40 MHz CCP discharge in pure H_2 and H_2:N_2=1:1 mixture were achieved.
- Sn can be almost fully removed from ML mirror surface for 10^{-20} min depending the discharge conditions.
- Etching rate of Sn in H_2:N_2=1:1 mixture is found to be lower in comparison with pure hydrogen indicating to the fact that H atoms are the main etcher of Sn.
- Some sputtering of Sn due to ion bombardment is also observed although the sputtering rate is rather low.
- On this reason it follows to verify quality of ML mirror surface after cleaning in CCP discharge.
- On this reason it is of interest to verify possibility of the rf discharge operation at the higher pressure as well as application of higher-rf discharges and molecular gases having the lower dissociation energy as, for example NH_3.

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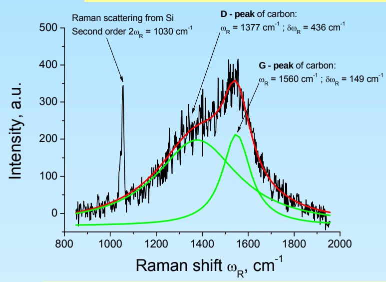
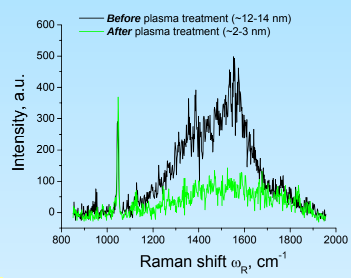
Cleaning of Mo:Si samples from C (results).

- **Analysis of C ML samples *before* and *after* the plasma treatment was carried out by using Raman spectroscopy of C-layer.**

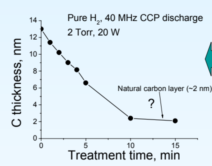


Raman spectrum of ~12 nm carbon layer on a C-covered ML mirror surface. Black curve – measured spectrum, green curves – Lorentzian deconvolution of the measured spectrum.

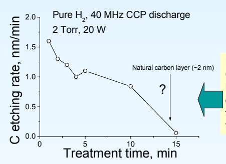


Raman spectrum of carbon layer on a ML mirror surface *before* and *after* plasma treatment.

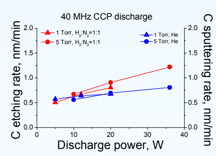
- **G-peak** (**G**raphite) corresponds to phonons of E2g symmetry according to basic vibrations of graphite lattice (in the graphite monocrystal there is observed the one rather narrow G-peak which splits onto G+ and G- peaks in case of the single-walled nanotubes).
- **D-peak** (**D**isordered carbon) in fact corresponds to phonons of other symmetry owing to distortions of graphite lattice mostly due to different defects, i.e. breaking purely graphite *sp2* C-C bonds and forming rather occasional C-C bonds particularly nearby the boundaries of the lattice.
- Both overlap and large widths of G- and D-peaks indicate presence of the disordered *sp2* C-C structure already on a scale of coordinated sphere (few inter-atomic distances, i.e. ≤ 1 nm) so that the structure of the carbon layer on a ML mirror surface can be designated as almost fully **amorphous *sp2* carbon**.



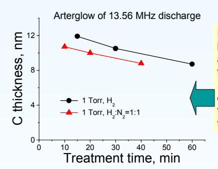
Reduction of the C layer thickness after cleaning the ML mirror samples in 40 MHz CCP discharge as function of treatment time.



Etching rate of C layer in 40 MHz CCP discharge as function of treatment time.



Etching and sputtering rates of C layer in 40 MHz CCP discharge as function of discharge power.



Reduction of the C layer thickness after cleaning in the afterglow of 13.56 MHz discharge as function of treatment time.

Summary

- C can be removed from a ML mirror surface, since the observed residual C layer ~2nm is apparently natural carbon.
- Etching rate of C in H_2/N_2=1/1 mixture is found to be compared to ones in pure hydrogen.
- Sputtering rate of C due to ion bombardment is found to be rather high and even greater the etching rate by H atoms. Most probably it occurs due to the essential amorphism of C layer.
- Therefore it would be important to study possibility of discharge operation at higher pressures that could give opportunities to overcome problems connected with the ion bombardment.
- To increase etching rate of C the gases with the lower dissociation threshold by electron impact, as for example NH_3, should be used.