Selective etching of Sn from Si- or Ru-capped EUV multilayer mirrors with Ar/Cl_2 plasma

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Motivation

The short wavelength (13.5nm) of EUV (extreme ultraviolet) light can make the resolution of the stepper higher so as to make a chip smaller, denser and faster. EUV lithography system is mainly composed of EUV light source and delivery system with EUV mirrors, which collect and deliver EUV light by reflection and focus it on to the wafer. For DPP (discharge produced plasma) source, grazing incident mirror collects EUV light whereas normal incident mirror collects EUV light in LPP (laser produced plasma) source. For grazing incident mirrors, a single layer can be used for total reflection up to the critical angle. Ru is the leading material for EUV mirror since the reflectivity is high. Ru is also used as a capping layer for normal incident mirror which is Si/Mo multilayer to have high reflectivity at a wavelength of EUV light under the Bragg condition. Thin Ru capping layer protects the structure of multilayer from fast ions and has a better oxide resistance than another capping layer material (Si). Therefore, Ru is the primary material exposed to EUV light source in either DPP source or LPP source. For EUV light source, tin (Sn) is one of advanced fuel candidates with higher conversion efficiency. However, easily condensable Sn will cause a serious ion debris build-up problem on the top surface of mirror. The debris on the mirror surface degrades the reflectivity of mirrors and accordingly shortens the life time of mirrors. In this study, a cleaning method for Sn debris build-up with Cl_2/Ar plasma etching will be discussed. In the previous work, plasma etching cleaning has been shown as a potential in-situ cleaning method to minimize time and effort to take out mirrors for cleaning. Compared to other cleaning methods, reactive ion etching with Cl_2/Ar plasma can remove Sn very fast (400 nm/min) with certain chemistry but it is the issue to remove Sn selectively from the mirror surface material. Therefore, in this study, the etch rates of Sn, Ru, Si and SiO_2 were measured and compared to investigate the affect of Cl_2/Ar plasma to the capping materials (Si or Ru) by changing chuck bias. Optimal gas mixture for reactive ion etching was studied. For more realistic cleaning test, Sn-deposited samples on Ru by evaporator were used to see how Cl_2/Ar plasma clean Sn off Ru surface.

Methods

Sn, Ru, Si, SiO_2 samples were etched by changing the bias voltage with RF power. The etch rate of each sample was measured with profilometer.

- Ru or Si is the capping layer material. SiO_2 was also considered since there is always a thin native oxide layer on Si.
- Masked half of sample with small piece of SiO_2 to see the etched depth.
- Etch time was 1min. for Sn (Sn is etched with the Chlorine plasma very quickly) and 10min for the rest of samples.
- All conditions except for bias were kept the same.
  500W ICP power, 10mTorr processing pressure,
  10 sccm Ar, 20 sccm Cl_2, ~2x10^{-7}base pressure
- Water pressure was minimized by baking out and checked using the RGA so as to reduce the depletion of chlorine atoms by water.

GALAXY chamber for Sn cleaning by reactive ion etching with Ar/Cl_2 plasma. It uses inductively coupled plasma (ICP) with internal coil inside of chamber.

Sn was deposited on Ru sample by a thermal evaporation method to investigate how cleaning works well in a more realistic situation.

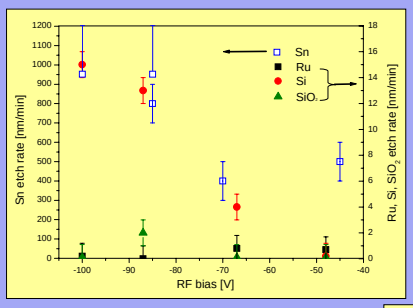
- 100nm thickness of Sn deposited on Ru with oxygen minimized.
- Etched with one of best recipes. All Sn is remove.

Bell jar evaporator used to make Sn on Ru sample by thermal evaporation

We examined "cleaned" Ru samples by Auger Electron Spectroscopy (AES) and compared reflectivity with a Xe DPP EUV light source (XCEED) here at UIUC

- After cleaning, the remaining Sn thickness on the Ru and the impact on the surface was studied by AES.
- Measured the grazing incidence reflectivity of pure the Ru sample, Sn-deposited Ru sample and 'cleaned' Ru sample to see if there is a reflectivity change among them.
- Obtained the signal strength of reflected EUV signal by placing three samples-'new Ru', 'Ru with 100nm Sn' and 'cleaned Ru'- at the same distance from the pinch and measuring the signal with a EUV photodiode. The signal was calibrated with a background signal and a reference signal. Total counts was calculated by summing up all the signal above the noise level.

Results



500W ICP power, 10mTorr
10 sccm Ar, 20 sccm Cl_2

Figure.1. The measured etch rates for Sn, Ru, Si and SiO_2 samples along various RF bias to the chuck. Left y-axis is used for Sn etch rate and right y-axis is for other materials since there is substantial difference between their etch rates. Reading error of depth measurement with profilometer was about ±100nm for Sn and ±10nm for other samples.

It is very promising that the Sn etch rate is substantially higher than other materials.

- Around -80V bias, reactive ion etching enhances the etch reaction significantly.
- With higher bias, even 1 min. cleaning etched all the Sn (~1μm thickness)
- Whereas Ru and SiO_2 do not etch much even for 10 min.
- For the case of Si, Ar/Cl_2 plasma reacts to form volatile silicon chloride($SiCl_4$) contributing to etching. There is some native oxide layer to lower the total etch rate.

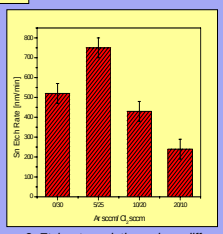


Figure.2. Etch rate variations along different gas mixture ratio with fixed pressure

Sn etching with different gas mixture ratio but same pressure was tested for better etch rate.

- Ar gas increases the chlorine radical density in the plasma and also increases the number of adsorption sites on the sample surface by bombarding and breaking the bonds of Sn.
- Etch rate is a complicated function of pressure, gas mixture, pumping speed, and so on.
- 5 sccm Ar and 25 sccm Cl_2 under 10mTorr showed the best etch rate of Sn in our system.
- With a help of Ar gas, we can etch Sn faster with less etchant gas (Cl_2).
- Cleaning speed (or etching rate) is much faster than other Sn cleaning method such as atomic hydrogen cleaning.

From the etch rate results, we see the possibility to etch Sn selectively from the top mirror surface, especially from Ru. Overetching may damage the Ru surface however the damage can be minimized by controlling the etching time and plasma density.

Will this cleaning really work for Sn on Ru?

- We applied one of best recipes (-77V, 5sccm Ar, 25 sccm Cl_2, 500W power, 10mTorr) for 5min. to clean off 100nm Sn on Ru.
- Figure.3. shows the cleaned Sn on Ru sample and the pure Ru sample. Small square part is the area covered by a piece of SiO_2.
- We did a Auger Electron Spectroscopy measurement to see if Sn remains after cleaning or if there is ion implantation.

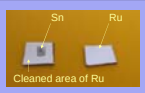
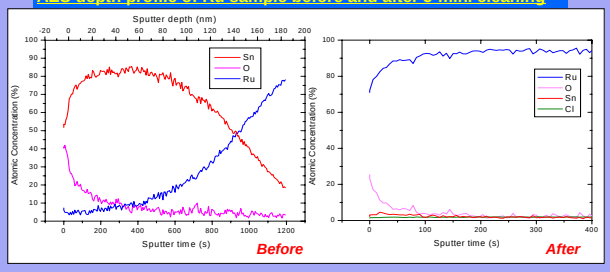


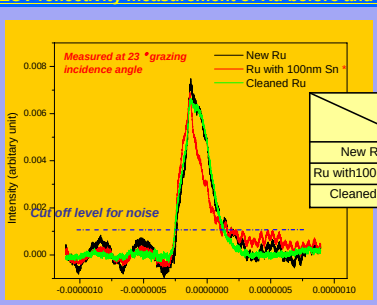
Figure.3. Cleaned Sn on Ru (left) vs. new Ru sample (right)

AES depth profile of Ru sample before and after 5-min. cleaning



- After cleaning, depth measurement by a profilometer showed that we etched Sn all the way down to the Ru surface as we intended. In order to check Sn cleaning, AES depth profile was used. Before cleaning, we had about 100nm Sn but after cleaning, Sn Auger electron signal was not detected on the surface. This confirms that we cleaned all the Sn off Ru.

EUV reflectivity measurement of Ru before and after cleaning



YES !

	Total counts (arbitrary unit)	Relative reflectivity to New Ru
New Ru	3.4	100%
Ru with100nm Sn	2.9	85.3%
Cleaned Ru	3.5	103%

**** 100nm Sn reflects more than a theory since sample holder may also reflect some EUV***

- The most concern with a cleaning is how much reflectivity recovers by cleaning. To see this, we compared EUV reflection of before- and after-cleaning samples to new Ru sample's by z-pinch EUV source in our group.
- 100nm Sn deposition degraded the reflectivity as much as 15%. But after cleaning, the reflectivity recovered to the original value. Total counts show reflection even improves.
- The measured reflectivity of 'Ru with 100nm Sn' sample was much higher than theoretical expectation. This might be caused by the reflection from other places such as sample holders.

Summary and future study

- Cl_2 plasma with some addition of Ar etches Sn much faster than Ru, which is a leading material for EUV mirror for both grazing incidence and normal incidence because of its high reflectivity and better oxidation resistance than Si.
- We cleaned Sn on Ru successfully with our recipe and confirmed there remains no Sn after cleaning with AES.
- Reflectivity comparison between '100nm Sn on Ru' and 'cleaned Ru' showed:
  - 100 nm Sn degrades EUV reflectivity of Ru considerably.
  - Sn cleaning with a plasma recovers the reflectivity fast and completely to the original value.
  - XCEED in our group can be well utilized for the study of EUV reflectivity.
- More study about cleaning affect to very thin (~2nm), real Ru capping layer for normal incidence multilayer mirror will be followed in the future.

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