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Event: SPIE Photomask Technology and EUV Lithography, 2017, Monterey, California, United States

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ABSTRACT EUV pellicles are needed to support EUV lithography in high volume manufacturing. We demonstrate progress in cap layer design for increased EUV transmission and infrared emission of the Polysilicon-film. In our research lab we obtained EUV transmission of 90% and good emissivity for a fully capped pSi film. We also discuss results on next generation EUV pellicle films. These include metal-silicides and graphite. Next-gen film performance is compared to the current generation pSi film. These films are expected to be stable at higher operating temperature than pSi. Metal-silicides have the advantage of sharing a similar process flow as that of pSi, while graphite shows ultimate high temperature performance at the expense of a more complicated manufacturing flow. Capping layers are needed here as well and capping strategies are discussed for these film generations.

1. THEORETICAL CONSIDERATIONS FOR PELLICLE FILMS

Pellicles are primarily developed for use in EUV lithography for logic[1] and product specifications and the nature of EUV absorption require that EUV pellicles are incredibly thin[2-10]. Not many materials allow 'good' EUV transmission[10] as seen in figure 1, which shows why Si was historically chosen as EUV pellicle film. Note that while Ru has fairly low EUV transmission, it is relatively stable under EUV and hydrogen conditions and can be used as IR emission enhancing cap layer. Note also that oxidation or oxygen impurities will negatively impact EUV transmission.

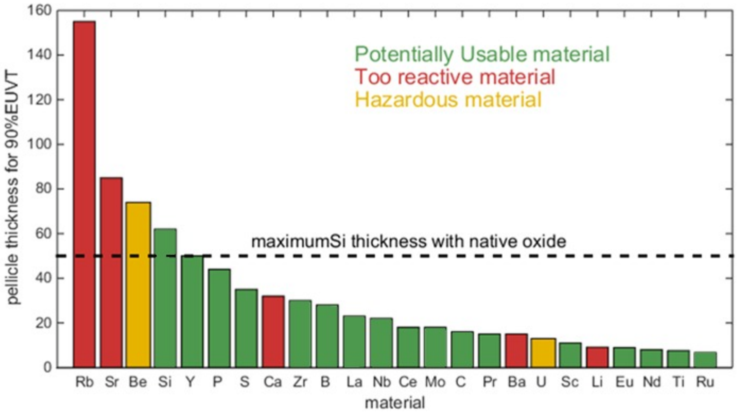

Figure 1: Materials thicknesses needed for 90% EUV transmission as obtained from CXRO[10] database.

Photomask Technology 2017, edited by Peter D. Buck, Emily E. Gallagher, Proc. of SPIE Vol. 10451, 104510O · © 2017 SPIE · CCC code: 0277-786X/17/$18 · doi: 10.1117/12.2280560

The <50nm thin pellicle film spans an area of >130cm^2 and resides just 2mm above the reticle. A minimum tension is required such that it does not get too close to the reticle. In practice pSi pellicle films must have a tension of the order of 100-200MPa and for other materials similar values hold. We aim for a yield strength that is 10x higher, hence around 1-2GPa. This value prevents that EUV pellicles are made of polymers, or of metals, because of low yield strength at high temperature. For this reason, spectral purity filters that suppress infrared consist of multilayer structures and not just pure metals[11]. It is well established in literature and shown in figure 2 that Si becomes ductile at high temperatures, and its yield strength becomes comparable to the required pre-tension. This limits the operating temperature of pSi based pellicle films in thermal cycling situations. In contrast, materials such as graphitic carbon, boron, SiN and metal silicides all have good high temperature mechanical properties even up to 1000°C. For mechanical reasons, the ductile to brittle transition temperature (DBTT), typically 2-3x lower than the melting temperature, is a realistic operational upper temperature limit for a pellicle.

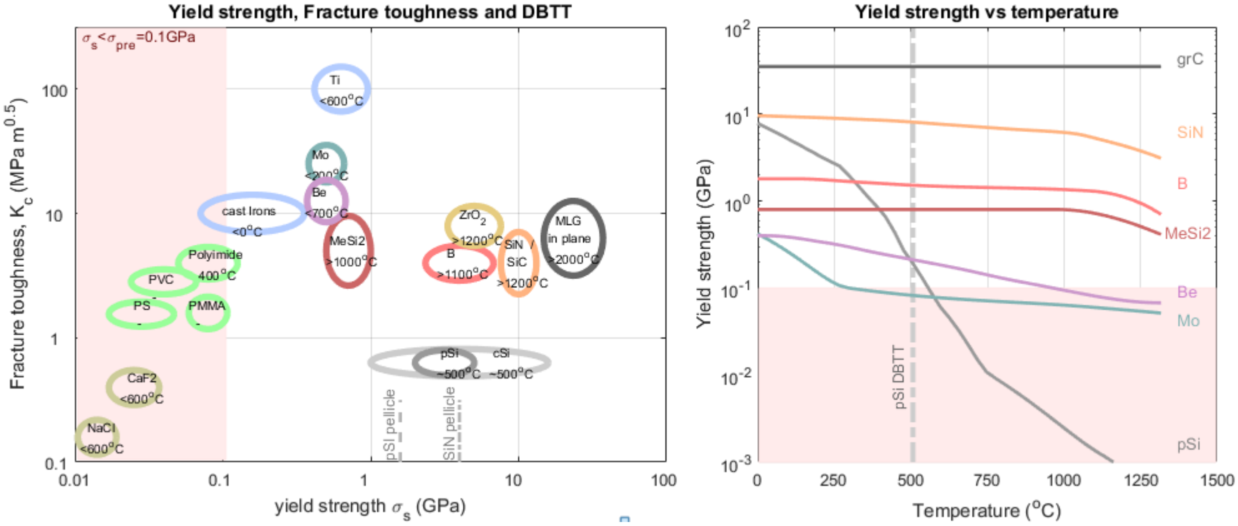

Figure 2: Left: Literature values for fracture toughness and yield strength of various materials. The temperatures indicate the ductile to brittle transition temperature (DBTT). Right: Yield strength of materials versus temperature. Most data provided here is for bulk materials, and serve an indicative role. The graphene/graphite (grC) data shown here is for very small samples[13].

EUV pellicles operate in near vacuum conditions. Although the contribution of cooling by the approximately 3Pa H_2 gas is not negligible, most absorbed heat is released by radiation. The needed infrared emission sets the requirements for the infrared optical properties of EUV pellicles. EUV pellicles should be semi-metallic, or have thin metal layers (figure 3). We note that thick metal layers reflect IR and hence give a low emissivity. It has been found[6] that the maximum emissivity that can be obtained for continuous sub-wavelength thin films is 0.5. Note however that emissivity goes to zero for grazing angles, so the angular integrated emissivity of a EUV pellicle is limited to a value close to 0.4. Knowing this we can estimate temperatures using the Stefan-Boltzmann's law. As an example, for an NXE3400 and a 250W source, typically a pellicle with 85-90% EUV transmission will absorb around 1-1.5W/cm^2 of EUV. If the film has emissivity of around 0.4, then the temperature reached is about 400-500°C.

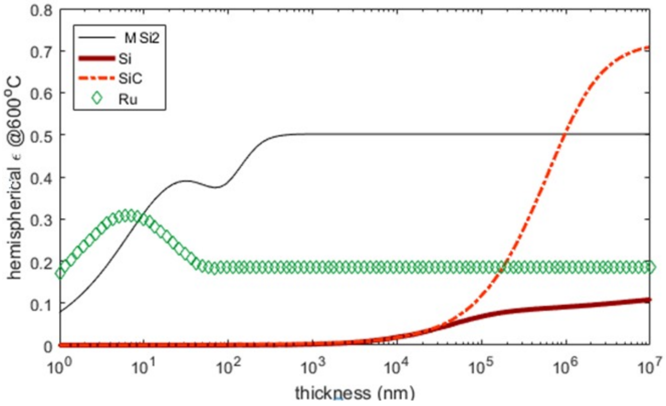

Figure 3: Emissivity of materials versus thickness based on literature bulk optical data. While the graph suggests maximum emissivity of 0.3 for Ru, in reality surface and grain scattering of electrons can give slightly different optical constants for ultrathin films[6] resulting in higher IR absorption/emission than thought possible based on bulk optical properties. For example with 2-3nm Ru it is possible to get to hemispherical integrated emissivity of 0.4 for real deposited films[6].

For critical dimension uniformity (CDU) control, EUV pellicles cannot reflect too much EUV to the wafer. While Si and SiN meet this specification, many materials that are interesting as emission enhancement or protective layers intrinsically reflect more than this (figure 4). For these materials it may be advantageous that they are deposited on a slightly rough surface, or in an anti-reflection configuration where the core or cap thickness is controlled to a multiple of 6.7 or 13.5nm. The tolerances depend on the amount of intrinsic reflection of the material in question.

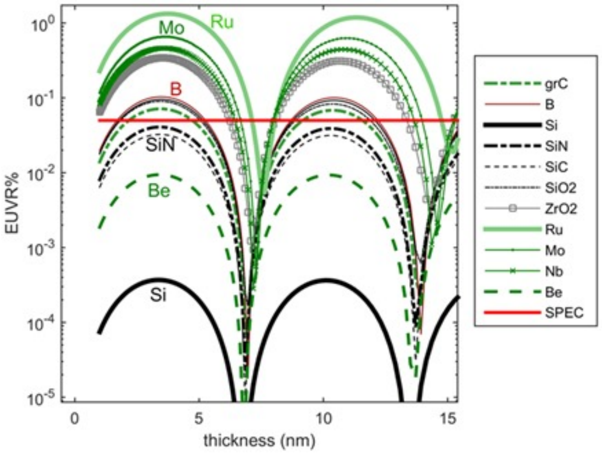

Figure 4: EUV reflectivity of materials versus layer thickness. While some materials may reflect too much EUV, also anti reflection conditions can be found by tuning the coating thickness. Some roughness can also reduce EUV reflection

Pellicle films are under tension and are not allowed to shrink under heat load, because that will increase the tension in the film. For a 1% shrink in the film the forces can already exceed several GPa as typical Youngs moduli are between 100 and 300GPa for films. A stress change of 100MPa can be tolerated, which translates in ~0.1% tolerable density change in the film during operation. No thin film characterization process can guarantee that the density of the film is that close to optimal (or bulk) values. In order to optimize the density of the pellicle film, the film will need to see temperatures during production that are similar to or higher than the expected operating temperature in the scanner. Offline heat exposures are needed to see if the films have the required stability. Figure 5 shows the result for films with good and too low density to illustrate what happens under exposure.

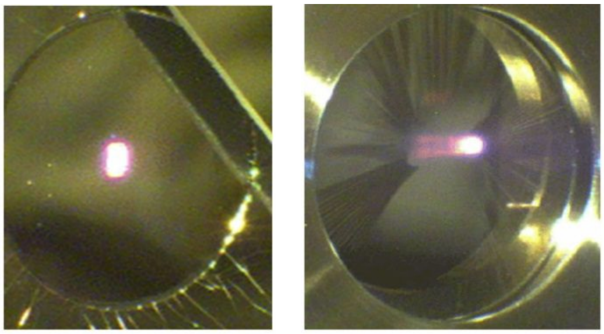

Figure 5: Left a pellicle film with good density under EUV exposure. Right a pellicle with too low density under EUV exposure will shrink. If the pellicle shrinks, local stresses can exceed several GPa and lead to tearing of the film. Film shrink is allowable only if it leads to tensile forces in the order of 100MPa, this means that volumetric shrink must be limited to the order of 0.1%.

2. FULLY CAPPED POLYSILICON FILMS WITH HIGH EUV TRANSMISSION

Current pSi based pellicles with SiN and Ru capping layers have EUV transmission around 80% and can support tools in the field. Higher source power can be supported by pSi based pellicles with improved EUV transmission. For the current pellicle with Ru cap this can be done by oxide removal after pellicle release, before cap deposition. Oxidation is undesired and has no function in the pellicle film. About 3-5% EUV transmission can be gained by removing the oxide (figure 6). Oxide can be removed without breaking vacuum just before the cap layer deposition, using vacuum based cleaning techniques. This can yield Ru capped pellicles with EUV transmission 83-85%. For higher EUV transmission it is necessary (figure 6) to use more transparent materials. We developed a new protective and emissive cap based on metal+Boron. Boron has very thin native oxide[12] as already shown by Luxel corp. in 1985. We have tested the potential of the Boron based concept on 1x1cm^2 samples. EUV transmission of >89% is experimentally obtained (fig. 7), and stability was assessed in EUV exposures (fig. 8) and heat load testing using lasers. Further thinning of the polysilicon film has resulted in EUV transmission beyond 90% on 1x1cm^2 samples, but scalability and use of a thinner pSi film in production has to be proven.

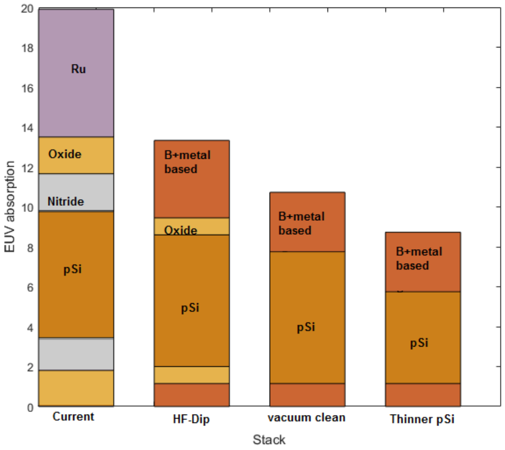

Figure 6: This graph shows were most EUV is lost in the pellicle film. Better EUV transmission can be gained by removing the (native and release process induced) oxide in current production films. Additional gains in EUV transmission can be obtained with B based capping layers. HF dipping before coating can remove excess oxide induced by the process. Oxide cleaning in vacuum is needed to also remove native oxide before cap deposition. A thinner pSi core is needed for EUV transmission beyond 90%.

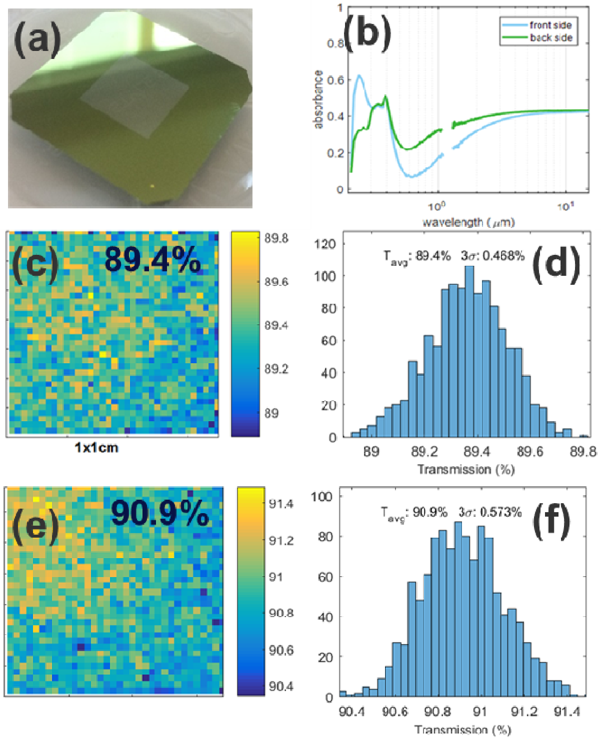

Figure 7: (a) Photo of 1x1cm^2 B/metal capped 40nm thick pSi film (b) IR-absorption/emissivity of film in fig. 7a. Asymmetric coatings and the Si-bandgap are responsible for the asymmetry in the front and backside VIS-IR absorption spectrum. (c, d) EUV transmission of film shown in fig. 7a. (e, f) With 30nm thick pSi and metal/B cap, more than 90% EUV transmission is obtained.

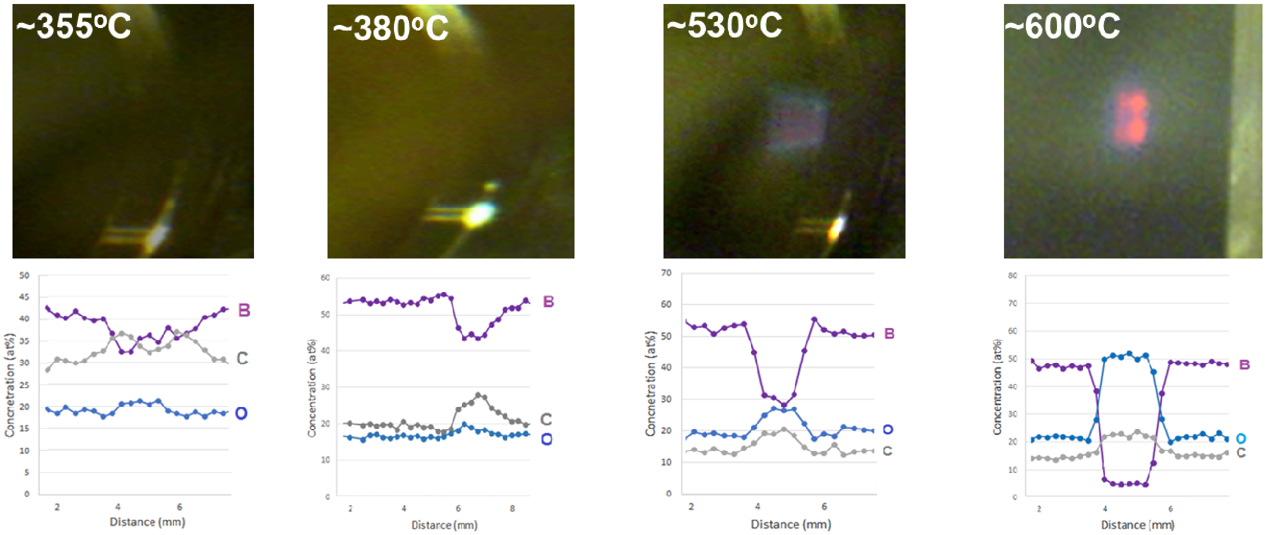

Figure 8: Stability of Boron under EUV conditions (full EUV dose over lifetime). Top: exposure photo, bottom XPS data. Heat load tests indicate that up to 450°C no B loss is detected (the dip in B signal seen in the left 2 graphs is due to carbon growth.) At 530°C some B loss is observed, but it is not sure if this is due to volatile B compounds or intermixing with the material below. Ru witness samples that are placed near the exposed 1cm^2 pellicle during exposure have never shown the presence of B. Pellicles with 89% EUV transmission and emissivity of 0.4 are expected to heat up to 450°C in the NXE3400 scanner with a 250W source.

3. METAL SILICIDE PELLICLE FILMS

Metal silicide films, which are inspired by work done in reference [11], share many of the good high temperature properties of SiN and SiC, but offer the advantage of an inherent high emissivity (figure 2, 3, 11). Inherent emissive pellicle films allow protective cap layers to be designed only for EUV+H_2 resistance. This is advantageous because most EUV transparent IR emission enhancing metals (except for Ru) oxidize easily so that use of metal emissive caps require more protective capping layers. In our tests we found that metal silicides can operate at over 650°C and offer approximately 2 times the EUV power of a metal capped polysilicon based pellicle while having similar EUV transmission (figure 11a,c). Although, for similar EUVT they need to be thinner than polysilicon, they are also stronger, so that in the end the robustness is comparable to polysilicon films. Unfortunately, most metal silicide films have higher thermal expansion coefficient than silicon resulting in thermal stresses during the annealing steps and in sacrificial layer deposition. The magnitude of the stress for early samples was 0.5xUTS (Ultimate Tensile Strength) and has prevented scaling, but process optimization lowered the stress to 0.15xUTS and now allows for scaling of these films (figure 9, 10). To optimize EUV transmission, the native oxide on the silicide film is removed using vacuum based cleaning, and then B based capping is applied. EUV transmission approaching 90% was obtained for fully capped metal silicide films. We believe further increasing EUV transmission is possible by altering the metal content in the silicide, without affecting the stress in the film. With this we expect the pellicle to be able to support source powers in the 250-500W range.

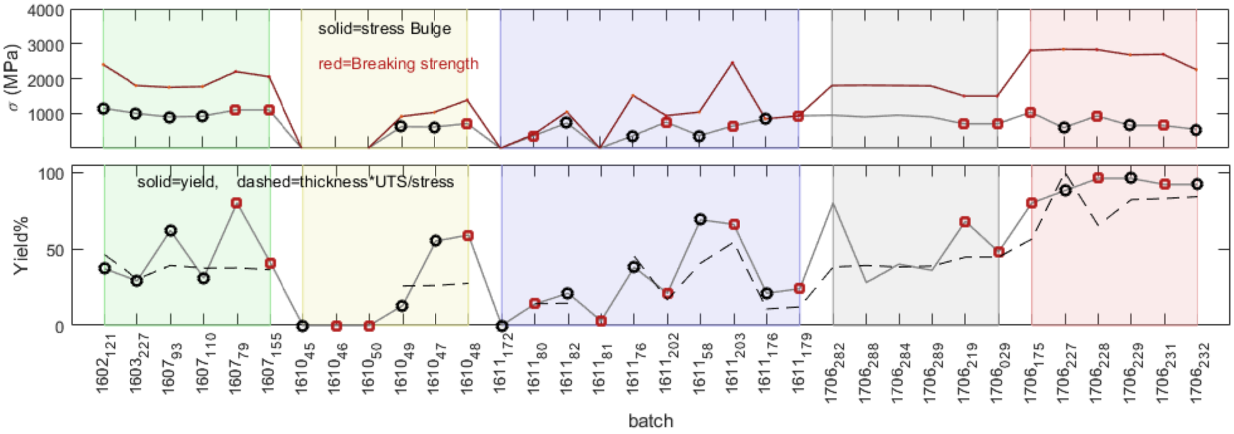

Figure 9: Evolution in time of metal-silicide development. Shown are yield, pre-tension (from Bulge) and average UTS of 1x1cm^2 pellicle films over time. Color areas indicate major recipe changes, in each area smaller changes are made in the recipe some of which are indicated by red squares or black circles. For the latest recipe the yield is almost 100%, breaking strength is close to 3GPa and pre-tension the lowest around 500MPa. These conditions allow scaling of the films. It is seen that the output yield of membranes and the simple formula thickness*UTS/stress follow a similar trend.

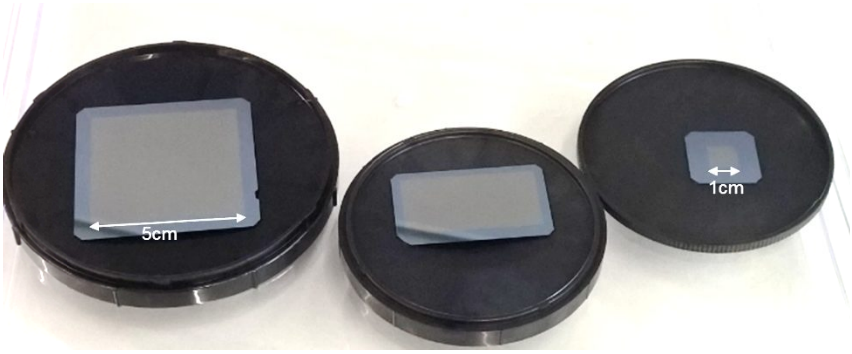

Figure 10: First larger scale (11 and 25cm^2) metal silicide samples

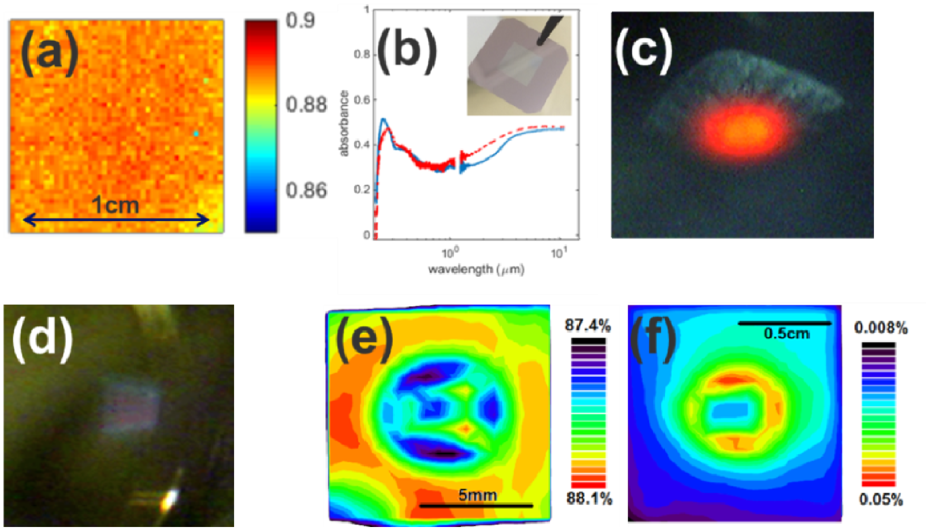

Figure 11: (a, b) EUV transmission and IR properties of 1x1cm metal silicide film. Inset (b) shows a photo of the sample. In (c) the membrane under heat load (5W/cm^2 absorbed) at 725°C is shown. Heat makes the membrane glow (red dot) and expand (wrinkles around the red dot). In (d) the film is shown under EUV exposure (2.1W absorbed/ 530°C), were post EUV transmission and reflection show only small changes in the film.

4. GRAPHITE BASED PELLICLE FILMS

Small (micron sized) samples of graphene or highly ordered graphite have shown incredible strength[13], making it an interesting candidate for EUV pellicle. Graphite is also inherently emissive just as metal silicides. An additional nice property is the absence of a solid native oxide after fabrication and film release, giving good EUV transmission. We have developed a process flow that does not involve manual transfer of films for highly ordered multilayer graphite. Membrane 6nm thick with sizes of 25x25mm^2 have been obtained. In our tests 6-12nm thick graphite films with 92-95% EUV transmission have shown the ultimate power load capability in vacuum up to 1800°C or 80W/cm^2 absorbed without problems (figure 12). However to this date our graphite films are mechanically fragile with respect to pSi and metal silicide films, preventing scaling (figure 13) and making research on protective capping layers, to protect from the hydrogen plasma (figure 14), difficult. We have concluded that a catalyst for graphite growth is needed that remains smooth and does not result in holes in the graphite film. The small holes cause local stress concentrations (figure 12). Smooth and uniform graphene/graphite growth is pursued by ASML and is also highly desired in the whole graphite and graphene field. With a smooth catalyst we believe that graphite pellicle films with up to 5-10GPa strength can be obtained. This then would make graphitefilms suitable for EUV pellicle.

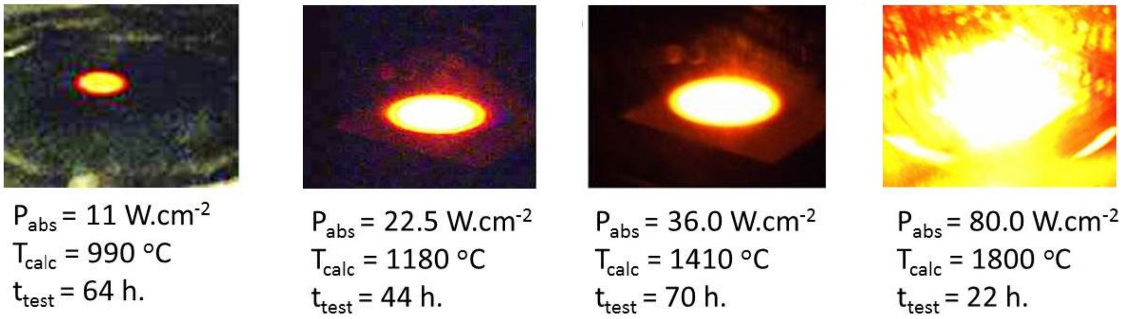

Figure 12: Heat load tests for graphene. Photos of glow, power absorbed, temperature and test-time are indicated. All samples survived these tests.

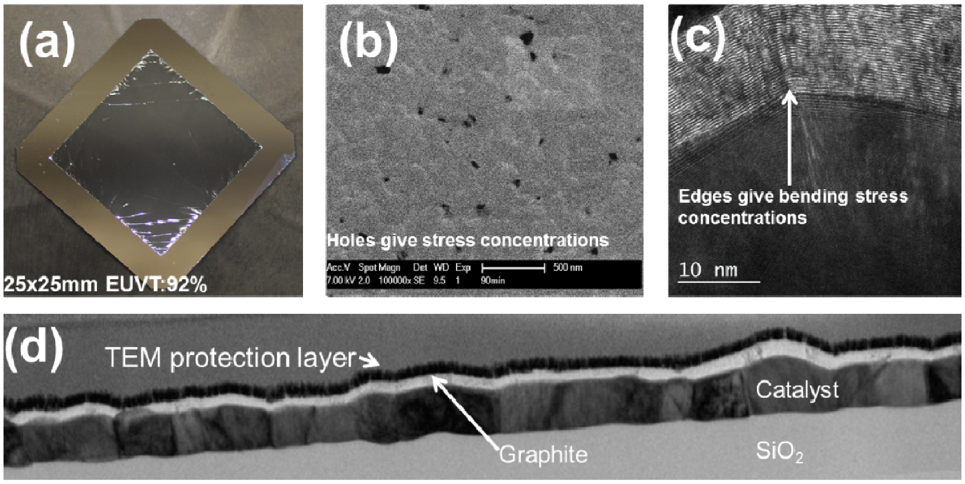

Figure 13: (a) Photo of a 25x25mm^2 graphite membrane. (b) SEM surface image of freestanding graphite. (c and d) TEM images of graphite as grown on the catalyst. Catalyst roughness and holes affect membrane performance and need to be solved.

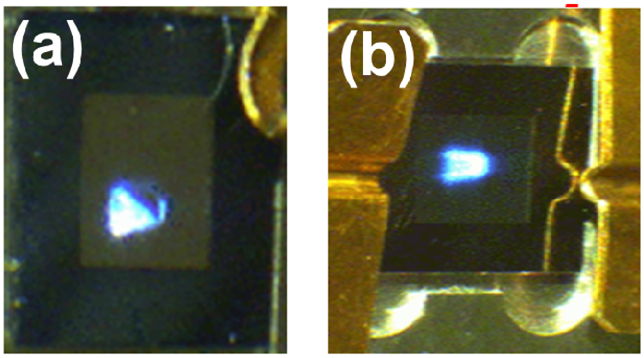

Figure 14: Graphite under EUV conditions (>250W equivalent source power). (a) Shows what happens without cap, in a hydrogen environment. In this case the membrane is etched and breaks after a while at the edge of the spot (here film stress is the largest). With a protective cap (b) or without hydrogen the membrane survives the test.

5. SUMMARY

Polysilicon films, with in vacuum oxygen removal and metal/Boron coatings have high EUV transmission of 89% or more and good emissivity. The cap remains protective to EUV+H_2 for the expected temperatures reached in the EUV scanner with a 250W source.

The metal silicide film is produced with a similar process as the pSi film and has around 2x the power capability of polysilicon and can support the EUV roadmap for higher source powers. High EUV transmission is also obtained for metal silicide films by using B based cap layers and vacuum based cleaning of native and manufacturing induced oxides.

For graphite based pellicles a CMOS flow was developed yielding 25x25mm^2 films with 92% transmission. Graphite pellicles have ultimate power load capability, however improvements are needed for the catalyst on which graphene is grown to increase strength before further scaling is possible.

6. ACKNOWLEDGEMENTS

The authors would like to thank to L. Sjmaenok from Phystex for discussions and teams at Philips Innovation Services and the XUV Optics Research group at the University of Twente for their contribution.

7. REFERENCES

[1] Turkot, B., et al. "EUV progress toward HVM readiness." Proc. SPIE. Vol. 9776. (2016) doi:10.1117/12.2225014

[2] Dhalluin F. et al, " Grid-supported EUV pellicles: A theoretical investigation for added value ", Proc. SPIE 9658, Photomask and Next-Generation Lithography Mask Technology XXII, 96580J (2015); doi:10.1117/12.2197454

[3] Scaccabarozzi L., Smith D.; Diago P. R.; Casimiri E.; Dziomkina N.; Meijer H.; "Investigation of *EUV Pellicle Feasibility"* Proc. SPIE Extreme Ultraviolet (EUV) Lithography IV, 867904 (2013) doi:10.1117/12.2015833

[4] Zoldesi C., et al. "Progress on EUV pellicle development.", SPIE Advanced Lithography, 90481N. (2014) doi:10.1117/12.2049276

[5] Goldfarb, D. L. "Fabrication of a full size EUV pellicle based on silicon nitride." Proc. of SPIE 9635. (2015) doi:10.1117/12.2196901

[6] van Zwol P.J. et al, "Emissivity of freestanding membranes with thin metal coatings", J. Appl. Phys. 118 213107 (2015) doi:10.1063/1.4936851

[7] Gao A, "Analysis of Extreme Ultraviolet Induced Surface Defect Process", Ph.D Thesis, University of Twente, Enschede (NL) (2015) ISBN: 978-90-365-3985-2

[8] Kim, S.G., et al. "Large-scale freestanding nanometer-thick graphite pellicles for mass production of nanodevices beyond 10 nm." Nanoscale 7, 14608 (2015) doi: 10.1039/c5nr03079j

[9] Pollentier, I., et al. "Novel membrane solutions for the EUV pellicle: better or not?." SPIE Advanced Lithography. 101430L (2017) doi:10.1117/12.2257891

[10] Henke B. L., Gullikson E. M., and Davis J. C.. Atomic Data and Nuclear Data Tables 54 181 (1993) doi:10.1006/adnd.1993.1

[11] Chkhalo, N. I., et al. "Free-standing spectral purity filters for extreme ultraviolet lithography." Journal of Micro/Nanolithography, MEMS, and MOEMS 11.2 021115-1 (2012). doi: 10.1117/1.JMM.11.2.021115

[12] Labov S., Bowyer S., and Steele G., "Boron and silicon: filters for the extreme ultraviolet" Applied optics 24, 576 (1985) doi: 10.1364/AO.24.000576

[13] Lee, C, et al. "Measurement of the elastic properties and intrinsic strength of monolayer graphene." Science 321 385 (2008) doi: 10.1126/science.1157996