NANOCOMPOSITE POLYMER PELLICLES FOR 157 NM PHOTOLITHOGRAPHY

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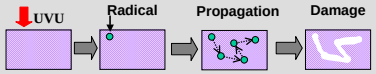
Objectives

- 157 nm proposed as the next wavelength for high resolution photolithography;
- The energy of incident photons in the VUV region is extremely high (10 times higher than that of infrared irradiation);
- Fluoropolymers used for pellicles at 248 nm and 193 nm wavelengths rapidly burst under irradiation with 157 nm light;
- The technology requires the development of new materials for reticle protection pellicles.

Photodegradation

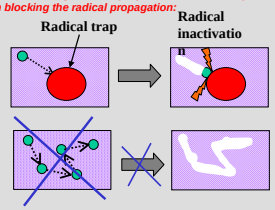
- Even diminutive (unavoidable) light adsorption by a pellicle will initiate photoinduced degradation process;
- The induced degradation process always involves photo-generation of radical species as initial steps;



- Adsorption of a high energy photon and the formation of a radical;
- Propagation of the radical with further degradation of polymer chains;
- One absorbed photon leads to many destroyed sites in the polymeric sample.
- The radicals initiate chemical reactions, which both degrade a polymer and generate more radicals;
- Radical propagating attack not only destroys polymer macromolecules but also forms unsaturated and conjugated products that adsorb 157 nm radiation;
- The degradation process becomes auto-accelerating in nature.

Free Radical Scavengers

Free-radical scavengers were proposed to retard the photodegradation through blocking the radical propagation:



- Organic scavengers traditionally used to improve photodegradation stability of polymers are not working, since they are adsorbing in 157 nm region;
- Inorganic particles of nanometer dimensions are proposed to be employed to trap radicals in fluoropolymers for pellicle applications;
- Incorporate nanoparticles made of a Cu(II) substance in a polymeric pellicle, because this material can effectively undergo reactions with radical species;
- Reaction of $CuCl_2$ with radicals proceeds according to the following scheme:

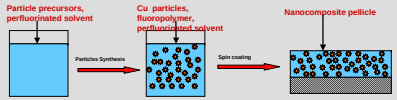
$$R\bullet + CuCl_2 \rightarrow RCl + CuCl$$

Specific objectives

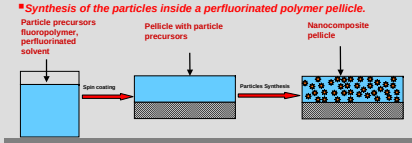
- Synthesize, characterize, and functionally evaluate a new nanocomposite material consisting of Cu (II) nanoparticles ranging in size from a few to 10 nm imbedded into thin flouropolymer films;
- Development of the reliable procedure for synthesis of Cu(II) nanoparticles;
- Development of methods for dispersing of nanoparticles in fluoropolymer media;
- Fabrication of nanocomposite pellicles;
- Optical and structural characterization of the pellicles;
- Mechanical and structural characterization of the pellicles after exposure to 157 nm radiation for various times;
- Evaluation of the pellicles for 157 nm photolithography applications.

Nanocomposite Pellicle Fabrication: Two Strategies

Synthesis of the nanoparticles initially in a solvents compatible with a fluorinated polymer used in pellicle fabrication.

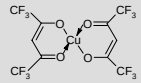


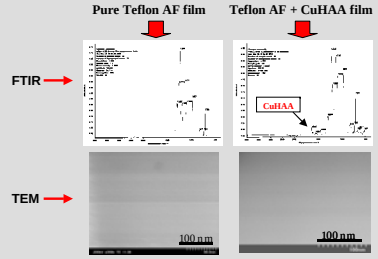
Synthesis of the particles inside a perfluorinated polymer pellicle.



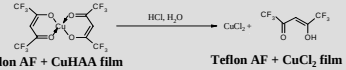
Strategy 1: Synthesis of nanoparticles inside pellicle

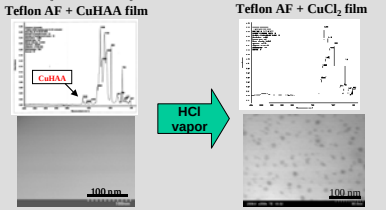
Copper (II) hexafluoro-2,4-pentanedionate (CuHAA) soluble in many fluorinated solvent was used to cast Teflon AF films, containing copper compound



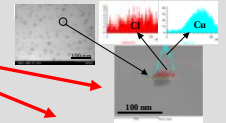


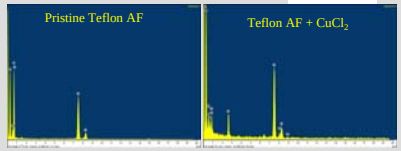
Synthesis of $CuCl_2$ particles inside pellicle





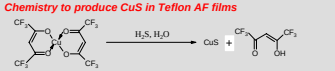
Energy Dispersive X-ray spectroscopy (EDX)



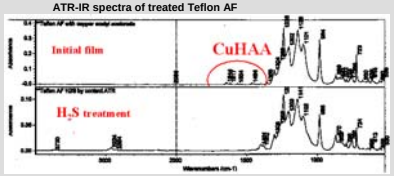


Synthesis of other Cu particles inside pellicle

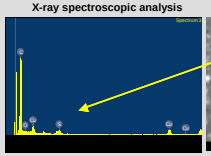
Chemistry to produce CuS in Teflon AF films



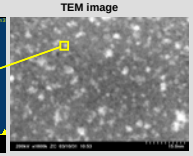
ATR-IR spectra of treated Teflon AF



X-ray spectroscopic analysis

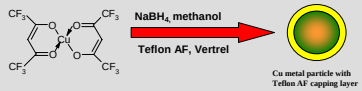


TEM image



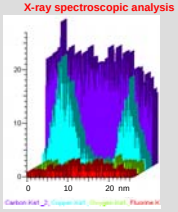
Synthesis of Cu particles in solvent

- Cu metal particles were synthesized directly in Vertrel® XF by chemical reduction;
  - CuHAA was dissolved in ca. 70mL of Vertrel® XF;
  - 2mL of a 1% Teflon AF solution was added ;
  - excess of $NaBH_4$ was dissolved in methanol and added to the copper solution with rapid stirring;
- Upon $NaBH_4$ addition mixture immediately becomes dark yellow and then a green-orange color due to the Ostwald ripening of the particles;
- Teflon coated particles quickly fall out of solution due to the insolubility of Teflon AF in Methanol.

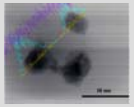


Cu particle characterization

X-ray spectroscopic analysis



TEM image



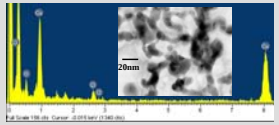
- Image is at a magnification of 1.1 million times showing particles approximately 7nm in diameter
- Mapping Energy Dispersive X-ray Spectroscopy shows copper metal particles in a fluorinated layer

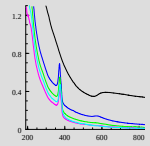
Conversion of Cu metal to $CuCl_2$ particles

Two methods:
- HCl vapor was bubbled into a suspension;
- thin Cu/Teflon AF films were exposed to HCl vapor;

Both methods yielded the same result.

X-ray spectroscopic analysis and TEM image

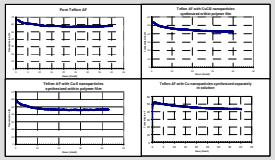




UV-visible spectroscopy shows the conversion of Cu metal to CCl_2

- Black curve is copper metal particles;
- With exposure to HCl vapor, copper plasmon band and background disappear and a new band appears at 390nm;
- This is most likely the charge transfer band of $CuCl_2$.

Transmissibility Data



Conclusions

- Two synthetic procedures were successfully developed for the inclusion of copper and copper (II) nanoparticles into Teflon AF polymer films.
- Both methods are simple, clean and easily scalable to production levels.