A Novel Filter Rating Method for less than 30 nm particle

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Abstract – This paper describes a novel filter rating method beyond the current 30 nm limit by combining dynamic light scattering (DLS) and ICP-MS technique, and proposes the usage of gold nanoparticle as the standard challenge particle. Furthermore, the effect of protective ligand addition was investigated in order to decrease the adsorbing effect between gold nanoparticle and membrane surface.

INTRODUCTION

As semiconductor device design rules continue to shrink, particle contamination control becomes increasingly important, driven by ever decreasing critical particle sizes on Si wafers. Finer filters are required to support increased demands outlined in the ITRS roadmap each year, and now 30 nm and finer rated filters are critical for leading-edge semiconductor manufacturing facilities.

Table 1 shows the comparison of various membranes with regard to rating and standard challenge species. Despite MF and UF membranes having already overlapped each other, different rating techniques are used. MF rating has been defined by particle removal efficiency using hard particles such as polystyrene latex spheres (PSL) . Meanwhile, UF rating is defined by challenging with proteins and vitamins using the molecular weight cut off (MWCO) concept. Considering that contamination control has been prescribed by particle size in the semiconductor industry, it is preferable to adhere to the MF particle based rating technique.

Table 1. Comparison of various membranes with regard to rating and standard challenge species.
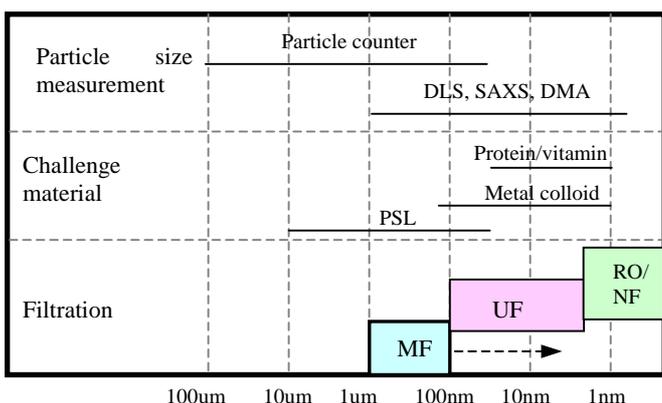
However, useful filter rating methods below 30 nm have not been reported. In general, filter ratings larger than 30 nm are typically defined by particle removal efficiency using laser light scattering particle counters and PSL as a standard challenge particle. But particle counting technology has reached a limitation for particles less than 30 nm in size due to the very low counting efficiency at these small sizes. Hence, we investigated alternative techniques and concluded combining DLS and ICP-MS with gold nanoparticle, as a challenge contaminant, was effective. Additionally, adding a protective ligand for reducing the adsorbing effect between particle and membrane surface was also examined.

EXPERIMENTAL

Gold nanoparticle

Gold nanoparticles (EMGC series, 10, 20 and 30 nm) supplied by British Biocell International, UK were suspended in dilutions of deionized water to test for efficacy as standard challenge particles. In order to decrease the adsorbing effect between the gold nanoparticle and the Polyethylene and Nylon6,6 membrane surfaces, ligands (stabilizer), Mercaptosuccinic acid (97%, Wako) and 2-amino-2-hydroxymethyl-1,3-propanediol (Wako), were used, respectively. For comparison, 33 nm PSL, 3030A, supplied by Duke Scientific, was also used in challenging these membranes.

Characterization

Particle size distributions (PSD) of challenge gold nanoparticles were measured with DLS (Zetasizer Nano ZS, Malvern, UK) installed with a semiconductor laser (wavelength = 532 nm) operating at an output power of 50 mW and an avalanche photo diode detector. Analysing the time-correlation function originated from the fluctuation of the scattered light, diffusion coefficient, D, can be obtained. Then, hydrodynamic diameter, d, is calculated by following Stokes-Einstein equation using solvent viscosity (η).

$$d = \frac{kT}{3\pi\eta D}$$

where k is Boltzmann coefficient, and T is absolute temperature in Kelvin [1]. Determining the quantity of gold was performed with ICP-MS (HP-4500, Agilent Technologies, US). In order to make a calibration curve, gold standard solution (HAuCl4, Wako, Japan) was used. Also, SEM observation was carried out with in-lens FE-SEM (S-5200, Hitachi, Japan) in order to cross-check the DLS result. To prevent size increases of the gold nanoparticle, any vapor depositions were not conducted prior to the observation.

Membrane

PTFE membranes of UltiKleen[TM] Excellar ER (filter rating 20 nm, Pall) filter and UltiKleen[TM] Excellar (filter rating 30 nm, Pall) filter were used. Ratings of 20 nm were estimated by extrapolation of the linear relationship between KL value, the critical pressure where isopropylalcohol (IPA) liquid film separates from the membrane pore, and reciprocal number of

rating in the range of 30 – 200 nm, obtained by challenge testing as shown in Figure 1. HDPE membranes of PE-Kleen UG001 (filter rating 10 nm, Pall) filter and UG003 (filter rating 30 nm, Pall) filter, Nylon6,6 membranes of Ultipleat[R] P-Nylon ANM (filter rating 20 nm, Pall) filter and AND (filter rating 40 nm, Pall) filter were also used for the proposed evaluation. Each membrane was cut into 47 mm diameter disks, and the filtration was performed by challenging with gold nanoparticle suspension after prewetting the membrane with IPA at the flow rate of 5 ml/min.
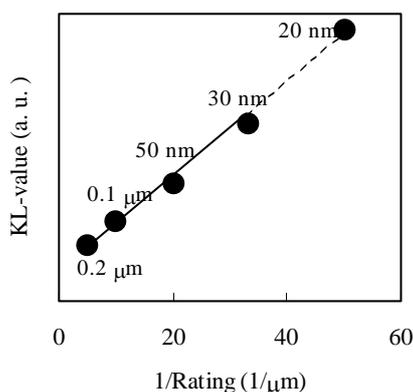

Figure 1. Correlation between KL-value and rating^{-1} of various PTFE filters.

RESULTS AND DISCUSSION

Particle size distribution

Figure 2 shows the particle size distributions of 10, 20, 30 nm sized gold nanoparticle measured with (a)DLS and (b)in-lens FE-SEM. PSL (33 nm) result is also shown in Figure 2(a). SEM image of the gold nanoparticles are shown in Figure 3. The sizes of each challenge material are roughly the same, and the mean diameters of gold nanoparticle and PSL determined by DLS measurement were 11.3, 21.6, 30.7 and 32.5 nm, respectively. The distribution of the PSL was a little broader than the gold nanoparticles.
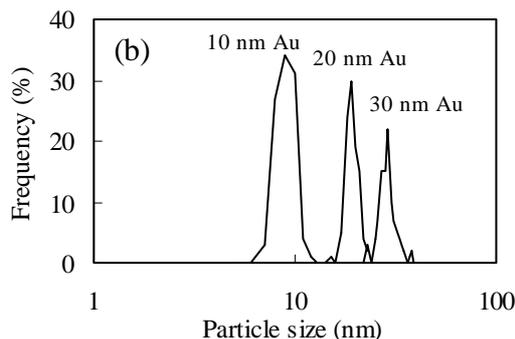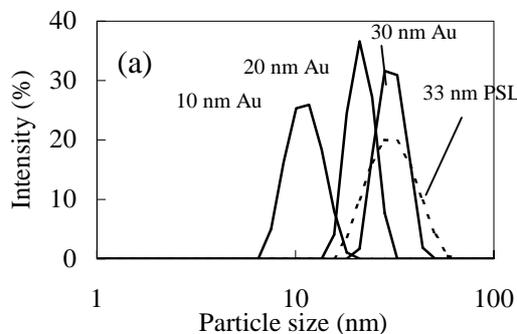

Figure 2. Particle size distributions of 10, 20, 30 nm gold nanoparticle and 33 nm PSL measured with (a)DLS and (b)in-lens FE-SEM except PSL (shown in Figure 3).
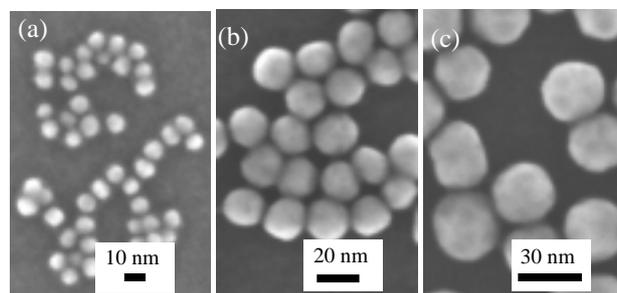

Figure 3. In-lens FE-SEM image of the (a)10 nm, (b)20 nm and (c)30 nm gold nanoparticles.

30 nm gold nanoparticle vs 33 nm PSL challenge test

Figure 4 indicates the removal efficiencies of Excellar ER (20 nm) membrane versus total particle concentration using the 30 nm gold nanoparticle and 33 nm PSL. Removal efficiencies by the both have nearly the same values, which are asymptotically close to 100% in the measured range.
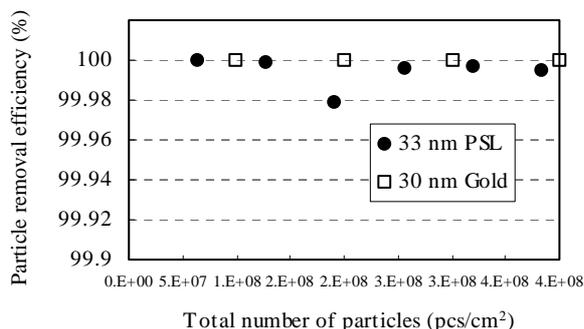

Figure 4. Particle removal efficiencies of Excellar ER (20 nm) membrane by 30 nm gold colloid and 33 nm PSL against challenged particle concentration.

Thus, the proposed rating method using 30 nm gold nanoparticle showed equivalent removal efficiency for 20 nm PTFE filter as compared to the conventional rating method using 33 nm PSL.

Evaluation of the Excellar and Excellar ER PTFE membrane

Figure 5 shows the result of applying the proposed method to Excellar ER membrane estimated as 20 nm by KL extrapolation method (Figure 1), using 0.5 ppm (3.5E+9 pcs/mL) suspension of 20 nm gold colloid, with the particle size confirmed as shown in Figure 2 and 3. Filter membranes of 30 nm rating showed lower removal efficiency, while the Excellar ER (20 nm) membrane shows more than 99% removal efficiency, as expected based on the membrane design.
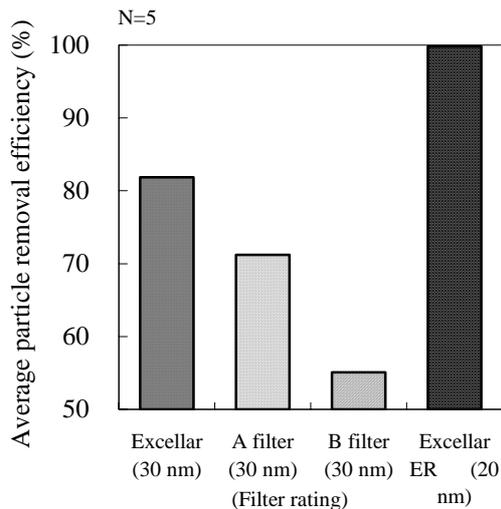

Figure 5. Average particle removal efficiencies of PTFE membranes measured using 20 nm gold colloid shown in Figure 2 and 3.

Effect of ligand addition for the reduction of adsorbing effect

Gold nanoparticle is generally prepared by the reduction of chlorauric acid ($HAuCl_4$) with citric acid acting as a stabilizer as well as a reductant agent [2]. The citric acid is physically adsorbed to the surface of gold, and it makes gold electrically stable in water [2]. As PTFE has very low surface energy, no interaction between the gold nanoparticle and the PTFE surface is expected. However, higher than expected particle removal efficiency might be found when challenging HDPE or Nylon6,6 membranes due to surface interactions. Hence, some protective ligands were investigated to reduce the attractive force between nanoparticle and membranes. It is known that the gold surface selectively adsorbs sulfer and nitrogen, and has a strong binding energy of Au-S estimated about 170 kJ/mol [3]. Therefore, the gold surface can be easily modified by thiol or amino functional groups, and various properties such as hydrophilic/hydrophobic and cationic/anionic can be added [4, 5, 6]. Investigating some protective ligands, we concluded that Mercaptosuccinic acid for HDPE and 2-amino-2-hydroxymethyl-1,3-propanediol for Nylon6,6, respectively, are very effective for reducing particle adsorption and eventually effective for reducing higher than expected particle removal efficiency. Figure 6 shows the result of particle removal efficiency with the addition of ligands to the gold nanoparticle dispersion liquid
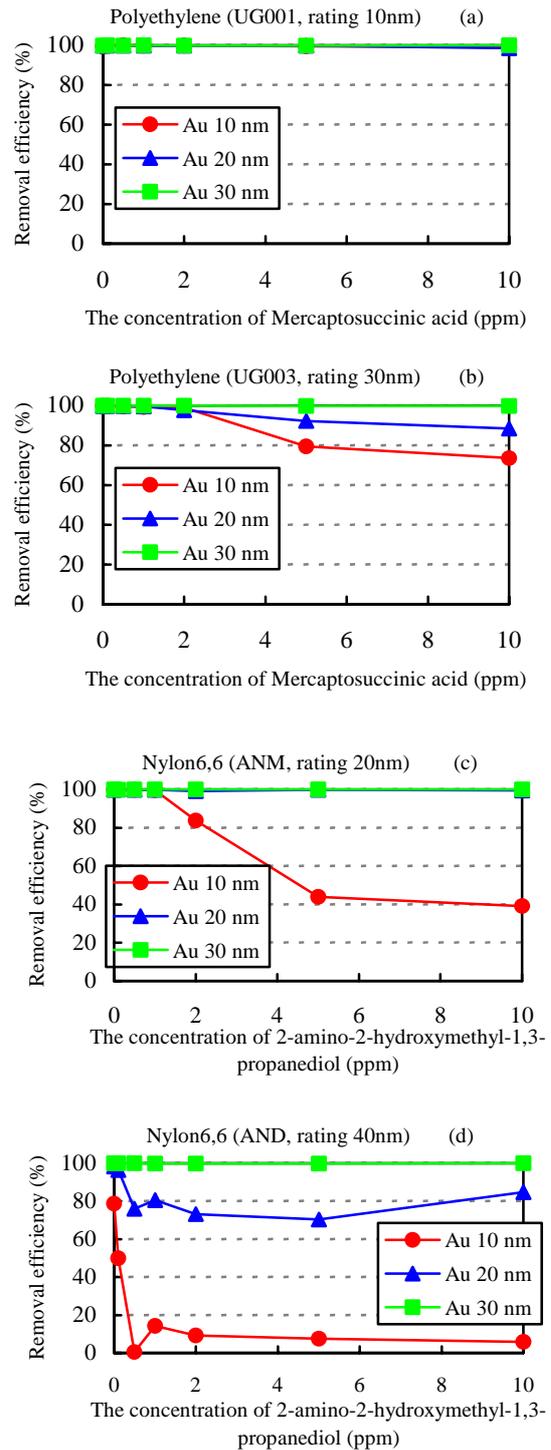

Figure 6. Particle removal efficiencies of polyethylene and nylon6,6 against 10, 20 and 30 nm gold nanoparticle with protective ligands.

at the various concentrations noted. On increasing the concentration of the ligands, the particle removal efficiencies of (b)UG003(30 nm) and (d)AND(40 nm) membranes were decreased and they approached certain values. On the contrary, (a)UG001(10 nm) and (c)ANM(20 nm) membranes have high removal capability even when challenging gold nanoparticle with a dense ligand concentration. Thus, this

result means that UG001 and ANM have high filtration removal capability against 10 nm and 20 nm, particles, respectively, without adsorbing effect. Schematic drawing of gold nanoparticle covered with protective ligands is shown in Figure 7.
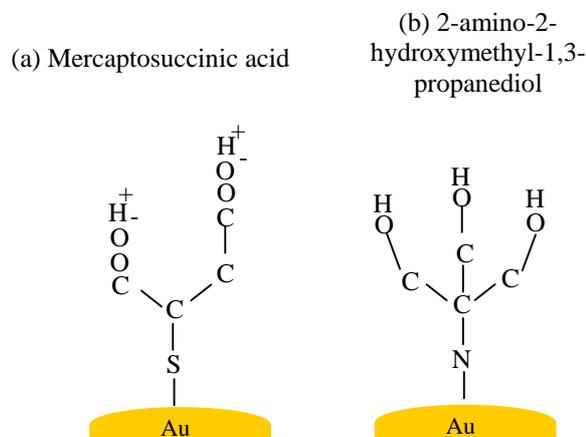

Figure 7. Schematic drawing of Au nanoparticle covered with (a) Mercaptosuccinic acid and (b) 2-amino-2-hydroxymethyl-1,3-propanediol.

Mercapto (thiol) group has a coordination linkage with the surface of the gold nanoparticle, and anionic carboxylate is negatively ionized in water. Amino group also has the same linkage as mercapto group with the gold surface. Zeta potential measurements, an optional function of DLS, were conducted with the 20 nm sized gold nanoparticles suspended with 10 ppm of their protective ligands (Table 2).

Table 2. Comparison of average zeta potential. (n=3)

Sample	Average zeta potential (mV) n=3
20 nm Gold only	-37.5
Gold + Mercaptosuccinic acid	-42.9
Gold + 2-amino-2-hydroxymethyl-1,3-propanediol	-52.9

Absolute value of zeta potentials using protective ligands were larger than that of gold nanoparticle only. This result clearly shows that the colloidal system covered with ligand becomes more stable than bare gold nanoparticle suspension. The surface zeta potentials of HDPE and nylon6,6 are also negatively charged at the near-neutral condition. Hence, the increase of repulsive force between particle and membrane can be expected, and consequently, this explains the decrease of removal efficiency which was observed, as seen in Figure 6. However, Mercaptosuccinic acid and 2-amino-2-hydroxymethyl-1,3-propanediol are only effective in terms of the removal efficiency reduction for HDPE and nylon6,6, respectively. Actually, no reduction of particle removal efficiency was observed when challenging Nylon 6,6 membrane with the gold colloid and Mercaptosuccinic acid

and the HDPE membrane with the gold colloid and 2-amino-2-hydroxymethyl-1,3-propanediol.

CONCLUSIONS

We developed a new rating method for finer than 30 nm filters by combining DLS and ICP-MS instrumentation with gold nanoparticle as a standard challenge suspension. Consequently, actual performance in terms of particle removal efficiency for finer than 30 nm rated membranes were demonstrated. DLS results regarding particle size distribution show good agreement with the result from in-lens FE-SEM observation. Additionally, some protective ligands were proven to be significant in order to reduce the particle-membrane attractive interaction.

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