

Study on the reactive nano carbon fine particles for SiC-CMP

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ABSTRACT

We have been developed reactive nano carbon fine particles to polish SiC substrate without strong oxidizing agents, plasma and UV light irradiation because the nano particles such as C₆₀ molecules appear the unique feature. The hybrid fine particles are formed by adsorption of the C₆₀(OH)_n n=ca.10 on the colloidal silica fine particles by the mixing process of the C₆₀(OH)_n n=ca.10/ KOH DIW solution adjusted by pH12. The hybrid fine particles can remove SiC materials because the C₆₀(OH)_n n=ca.10 have the electron affinity. The MRR drastically increase by mixing H₂O₂ additive and C₆₀(OH)_n n=ca.10 KOH DIW solutions although the slurries using each additive are low removal rate. As the higher concentration of the C₆₀(OH)_n n=ca.10 solute, the MRR become higher. In this case, chemical reaction by OH radical from H₂O₂ additive might be accelerated by C₆₀(OH)_n n=ca.10 molecules because these molecules are electron acceptor that called radical sponge.

INTRODUCTION

The SiC substrate is widely applied to power device for Hybrid car, Electric car and train, because this material has low dielectric loss, high stand voltage and thermal stability. To expand the SiC power devices, productivity and cost reduction need to improve on the fabrication process including substrate fabrication process. Especially, lapping and polishing process of the substrate is key process to realize high throughput and cost reduction⁽¹⁾. Recently several studies on the high efficiency SiC polishing methods have been reported as plasma-assisted polishing, UV light irradiation method, electric applied methods and CARE (CAlyst-Referred Etching) method⁽²⁾⁻⁽⁵⁾. In these cases, the structures of the polishing devices need to change on these processing principles from the conventional CMP devices. For the slurry and polishing pads, high performance slurry using potassium permanganate (KMnO₄), Dilatancy pad and LHA have been developed⁽⁶⁾⁻⁽⁹⁾.

In previous study, we had studied nano unique feature at the region the less than 20nm diameter on the colloidal silica fine particle as the higher efficiency removal feature on the sapphire substrate and formation of hybrid fine particles composed of large size core silica particles and small size silica particles⁽⁹⁾⁽¹⁰⁾. In these cases, the Hybrid fine particles by two kinds of colloidal silicas can be polished as the high removal

rate and smooth polished surface. We also have been studied the hybrid fine particles using Hydroxylated fullerene to applied the sapphire substrate and Cu⁽¹¹⁾⁽¹²⁾. The C60 molecules have hard cage structure like soccer ball shape that have high symmetry and high reactivity to accept electron in the molecule. Especially, number of the OH groups on Hydroxylated fullerene is important factor to determine polishing performance⁽¹²⁾. In the case of the sapphire substrate, material removal rate of the Hydroxylated fullerene having OH=12 is the higher than the Hydroxylated fullerene having OH=36 although material removal rate of Cu-CMP is opposite⁽¹³⁾. This feature predicts Hydroxylated fullerene having OH=12 has higher hardness of the cage structure than Hydroxylated fullerene having OH=36 because of double bond remain between carbon atoms on the cage structure without chemical attack by OH groups.

In presents report, we focus on the Hydroxylated fullerene having OH=ca.10 because these types of the Hydroxylated fullerene might be the almost the same as OH=12 and can be produced large amount of the materials by frontier carbon company. In this case, Hybrid fine particle by Hydroxylated fullerene and colloidal silica slurry is evaluated by the SiC-CMP performance. In this paper, we discuss that possibility of the Hybrid fine particles using Hydroxylated fullerene on the SiC-CMP.

EXPERIMENTAL

Figure 1 shows preparation flow of the Hydroxylated fullerene KOH solution with USW-wave and mixing process under the constant pH12. Hydroxylated fullerene powder was used C₆₀(OH)_n n=ca.10 (nanom spectra D100, frontier carbon co., ltd.) in our study. USW and mixing process time is 1 hour respectively. After this dissolution process, Hydroxylated fullerene KOH solution of transparency is dark brown color. The Hydroxylated fullerene KOH solution was mixed with colloidal silica slurries (PL-3 Fuso chemical co. ltd.). Concentration of the C₆₀(OH)_n n=ca.10 in the mixed slurry was adjusted at the region from 0.01wt% to 0.05wt%.

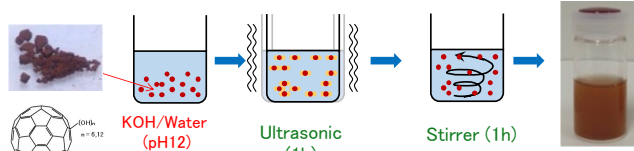
After the mixing process, fine particles as the colloidal silica and the C₆₀(OH)_n n=ca.10 is observed by TEM (JEM-F200, JEOL). In the TEM observation, accelerating Voltage of the electron beam is set by 200kV. TEM Sample is prepared by drying process from the slurries on the TEM microgrid (STEM Cu 150P Oken shoji Co. Ltd) in the Vacuum.

The polishing test is performed by Rana-30 (IMT corporation) and is used SUBA600 as shown in Figure 2. Polishing pressure is adjusted to 4.87psi and rotation speed of the polishing head and platen is set to 60rpm respectively. The mixed slurry is dammed by the container attached with platen.

RESULT AND DISCUSSION

Figure 3 show that TEM images of the colloidal silica and hybrid fine particles on the TEM sample preparation. In the case of the hybrid fine particles, some round shape contrast as the same C60 cage size appear against the image of the colloidal silica fine particles. The diameter of the hybrid fine particle increases around several nm by adsorbing the C₆₀(OH)_n n=ca.10 molecules. This particle can be estimated several layers adsorption of the C₆₀(OH)_n n=ca.10 on the silica particles. In this case, the presence of unevenness on the adsorption surface layers was observed.

1. Dissolution of $C_{60}(OH)_n$ $n \approx 10$ (Hyd.C₆₀)



2. Hybrid slurry fabrication using Colloidal Silica slurry (PL3)

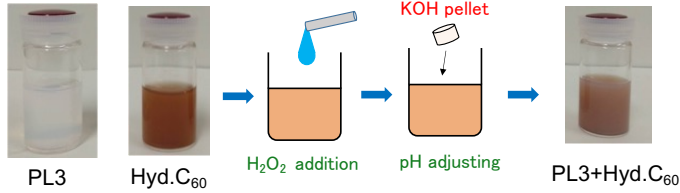


Figure.1 Process of the mixed slurry fabrication.
Hyd.C60 stand for $C_{60}(OH)_n$ $n \approx 10$

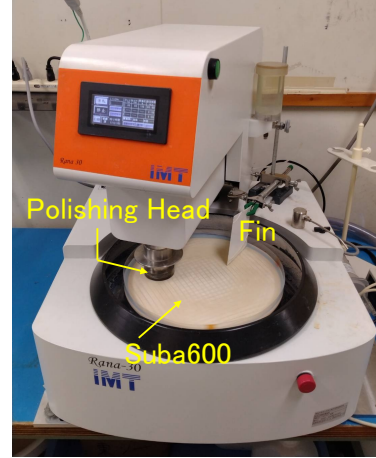
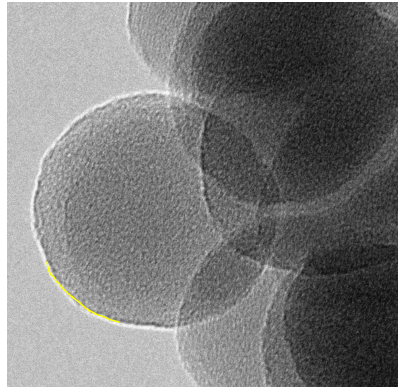


Figure.2 Polishing device.

(a) Colloidal silica



(b) Hybrid fine particle

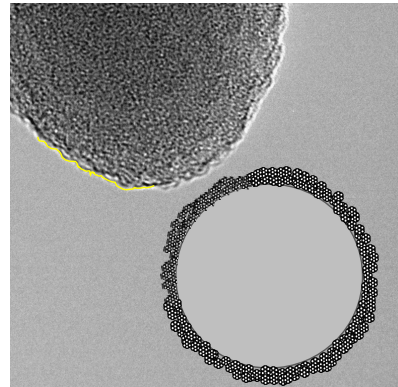


Figure.3 TEM images and surface lines of (a) colloidal silica nano particles and (b) Hybrid fine particle with $C_{60}(OH)_n$ $n \approx 10$. Figure.3 (b) indicate that model of the hybrid fine particle in the TEM picture.

Figure 4 show material removal rates on the SiC substrates at the case of H_2O_2 additive and mixing the $C_{60}(OH)_n$ $n \approx 10$ solution. In this experiment, polishing pressure is adjusted around 4.87psi and rotation speed of the polishing head and platen is set from 60rpm. Polishing pad is used SUBA600 without groove. At the case of the only silica slurry, the MRR (Material Removal Rate) is almost zero because the hardness of the SiC substrate is harder than that of silica fine particles. At the H_2O_2 addition (5wt%) to the colloidal silica slurry, the MRR is 3.4nm/h in this condition. In the case of the $C_{60}(OH)_n$ $n \approx 10$ solution without H_2O_2 additive, the MRR is almost the same as H_2O_2 additional condition. This result predicts that the $C_{60}(OH)_n$ $n \approx 10$ might be appeared chemical reactivity against SiC materials. After mixing H_2O_2 additive to the mixing slurry of the silica and $C_{60}(OH)_n$ $n \approx 10$ solution, the MRR become higher until 24.2nm/h. These results indicate that the $C_{60}(OH)_n$ $n \approx 10$ molecules might be highly reactive material to SiC substrate. This result predicts that the possibility of the reactive nano carbon fine particles using the $C_{60}(OH)_n$ $n \approx 10$ molecules combined with colloidal silica fine particle to apply the SiC-CMP.

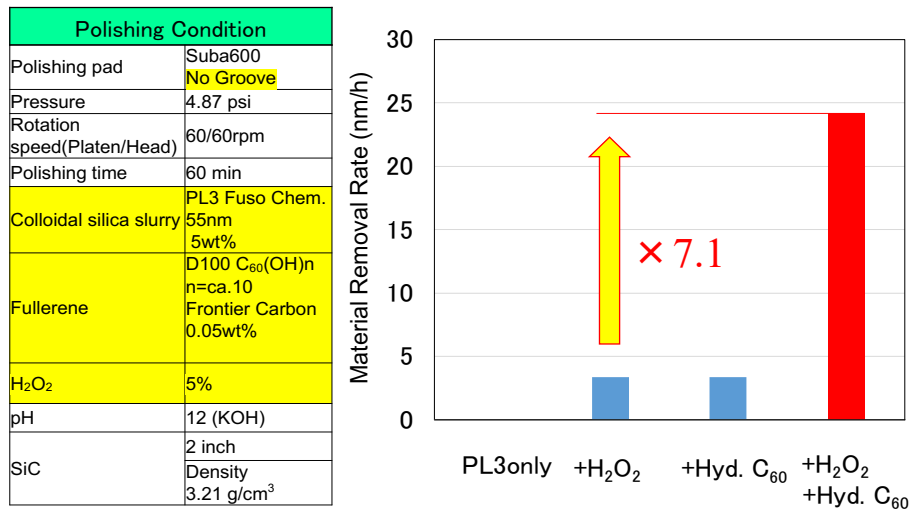


Figure. 4 Material Removal Rate of the SiC-CMP at the case of H₂O₂ addition and the C₆₀(OH)_n n=ca.10 /KOH solution mixing.

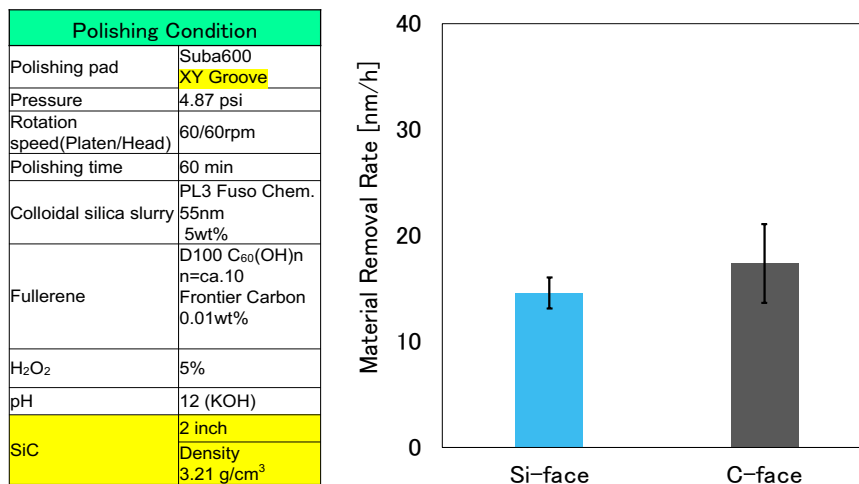


Figure.5 Material Removal Rate of the C-face and Si-face

Figure 5 show the MRR of the C-face and Si-face. In the case of the hybrid particles, The MRR of the C-face is the higher than that of Si-face. This result indicated that a carbon allotrope as the C₆₀(OH)_n n=ca.10 molecules might be adsorbed or reacted to the C-face.

Figure6 shows that dependence of the H₂O₂ concentrations on the MRR. In this case, the MRR increase as the concentration of the H₂O₂ become higher. On the concentration of the Hydroxylated fullerene, The MRR increase drastically as the higher concentration as shown in figure 7. In this time, sediment in the slurry did not find after polishing. Figure 8 shows that the model the material removal mechanism on the reactive hybrid fine particles. In the case of C-face, adsorption of the Hydroxylated fullerene promotes to the SiC substrate because the MRR of the C-face become higher. In this case, chemical reaction by OH radical from H₂O₂ additive is accelerated by

$C_{60}(OH)_n$ $n \approx 10$ molecules because this molecule is electron acceptor called radicals sponge⁽¹⁴⁾⁻⁽¹⁶⁾.

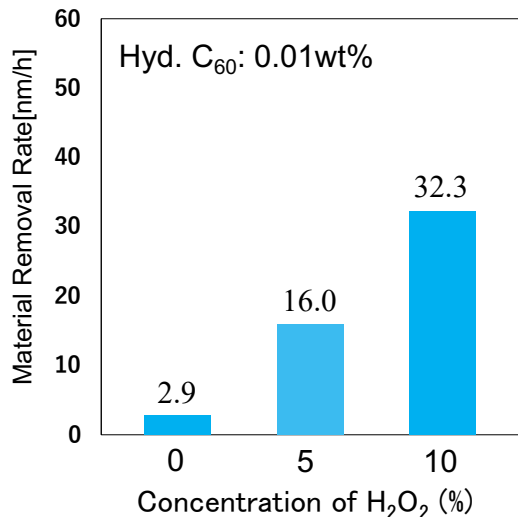


Figure.6 H₂O₂ concentrations

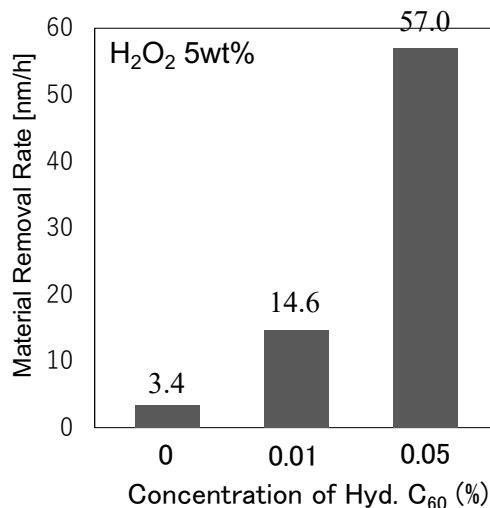


Figure.7 $C_{60}(OH)_n$ $n \approx 10$ concentrations

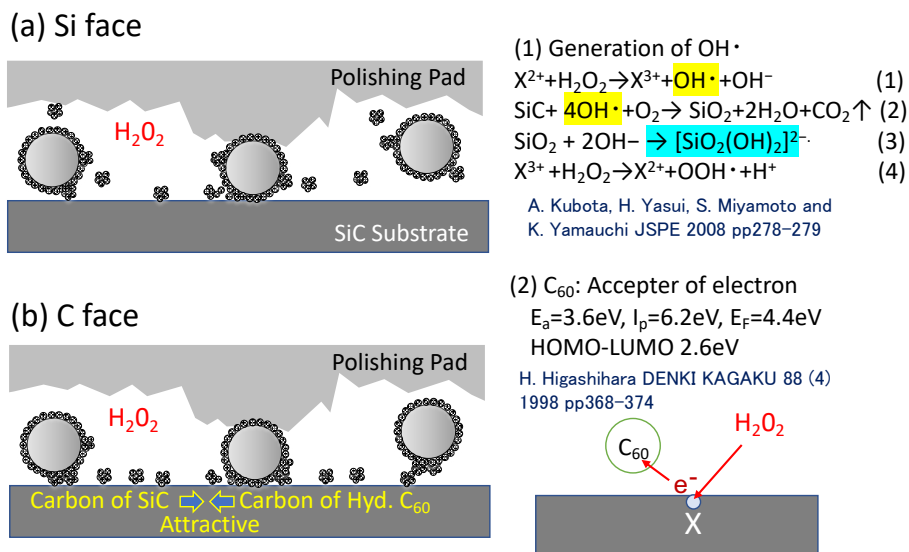


Figure.8 Material Removal Mechanism at the case of Hybrid nano particle.

CONCLUSIONS

TEM images indicate that the hybrid fine particles are formed by adsorption of the $C_{60}(OH)_n$ $n \approx 10$ on the colloidal silica fine particles by the mixing process of the $C_{60}(OH)_n$ $n \approx 10$ / KOH DIW solution adjusted by pH12. The hybrid fine particles can remove Si-face and C-face of the SiC wafer because the $C_{60}(OH)_n$ $n \approx 10$ has the electron affinity. The MRR increase drastically by mixing H₂O₂ additive and $C_{60}(OH)_n$ $n \approx 10$ KOH DIW solution although the slurries using each additive are low removal rate. As the higher concentration of the $C_{60}(OH)_n$ $n \approx 10$ solute, the MRR become

higher. In this case, chemical reaction by OH radical from H₂O₂ additive might be accelerated by C₆₀(OH)_n n=ca.10 molecules because this molecule is electron acceptor called radical sponge. In future, we need to evaluate KMnO₄ additive instead of H₂O₂ and UV light irradiation, during polishing and polymerization of C₆₀ to increase the MRR (17)-(19).

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