

Y₂O₃ nanosheets as slurry abrasives for chemical-mechanical planarization of copper

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Abstract: Continued reduction in feature dimension in integrated circuits demands high degree of flatness after chemical mechanical polishing. Here we report using new yttrium oxide (Y₂O₃) nanosheets as slurry abrasives for chemical-mechanical planarization (CMP) of copper. Results showed that the global planarization was improved by 30% using a slurry containing Y₂O₃ nanosheets in comparison with a standard industrial slurry. During CMP, the two-dimensional square shaped Y₂O₃ nanosheet is believed to induce the low friction, the better rheological performance, and the laminar flow leading to the decrease in the within-wafer-non-uniformity, surface roughness, as well as dishing. The application of the two-dimensional nanosheets as abrasive in CMP would increase the manufacturing yield of integrated circuits.

Keywords: Y₂O₃ nanosheets; chemical-mechanical planarization (CMP); nanoabrasives; slurry flow; wafer-pad contact

1 Introduction

Chemical mechanical planarization (CMP) has been used as a major process step for manufacturing integrated circuits in last three decades [1]. Significant effort has been made in developing new and effective slurries [2, 3]. To date, global planarization remains to be a major concern [4], particularly for patterned wafers where the metal/dielectric density differs across the wafer. The limitation of ion and slurry transfer is one of the key factors affecting planarization. The planarization is characterized by the within-wafer-non-uniformity (WIWNU) [5, 6]. Previous studies in this regard have been focused on optimization of polishing parameters and utilization of corrosion inhibitors [7–10]. It is always desirable to develop a slurry that improves the slurry transport and contact between the polishing pad and the wafer surface.

We have recently reported that using boron oxide nanoparticles (NPs) the materials removal rate was increased during copper (Cu) CMP [11]. In this study, we focus on mechanisms of planarization. We report a new CMP slurry containing yttrium oxide (Y₂O₃) nanosheets (NS) as abrasives leading to improvement in promising efficiency. For comparison, planarization processes using a commercial colloidal silica (SiO₂) slurry were studied. The mechanism of planarization was studied via friction performances and dynamic behaviors under a fluid shear. Two-dimensional Y₂O₃ NS abrasives prompt an alternative solution to improve the wafer planarization during CMP.

2 Experimental

2.1 Materials

The citric acid, benzotriazole (BTA), and hydrogen peroxide (H₂O₂) used in this study were purchased from Sigma-Aldrich (USA) and were used without

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further purification. A home-made abrasive, Y_2O_3 NS (~16 nm thick and >200 nm side, see Fig. S1 in Electronic Supplementary Material) was used to prepare CMP slurry. The Y_2O_3 NS was synthesized via a hydrothermal method, and those results will be reported elsewhere. The home-made slurry was composed of citric acid (0.01 M), BTA (0.05 wt%), H_2O_2 (3 vol%), Y_2O_3 NS abrasive (3 wt%), and deionized (DI) water.

A commercial SiO_2 slurry (~Ø 35 nm, Fujimi Corporation) was used as-received for comparison in CMP. Another SiO_2 NPs filtered from a commercial slurry (~Ø 35 nm, Cabot Electronics co.) with the same particle size and shape were used in friction and rheological experiments. Unwanted chemicals in the slurry were removed by filtering and rinsing with DI water for three times. The thoroughly rinsed SiO_2 NPs were collected after drying at 40 °C for 24 h for future friction and rheological experiments.

Cu film (2 µm thick) coated silicon (Si) wafers (Ø 300 mm) were used as target substrates for CMP experiments. These wafers were then CMPed with an IKONIC™ polishing pad (Rohm & Haas).

2.2 CMP experiment and Characterizations

All polishing experiments were conducted using a universal CMP tester. Polishing was conducted for 1 min. Wafers were placed face-down onto the polishing pad. The applied pressure was 1 psi (6894.757 Pa), and rotation speeds of the pad and the wafer were maintained at 79 rpm and 76 rpm, respectively. The speeds were kept close to each other for good uniformity in wafer planarization. Each slurry was used to polish four wafers.

Frictional behaviors and rheological properties of the slurry were examined. In order to solely investigate the frictional behaviors and rheological properties of SiO_2 NP and Y_2O_3 NS, the measurements were conducted in DI water. Friction experiments of Cu wafers were carried out using a tribometer (CSM Instruments). IC1000 polishing pads (Rohm & Haas) with SiO_2 (3 wt%) and Y_2O_3 (3 wt%) slurries were used in friction experiments. Friction coefficients were recorded during each test for 60 cycles (20 mm per cycle, 20 mm/s) with an applied pressure of 80 kPa. An AR-G2 rheometer (TA Instruments) was used to measure the change of shear stress with shear rate ranging from 30 s⁻¹ to

500 s⁻¹. In rheological experiments, three different concentrations were selected for slurries, 0.3 wt%, 3 wt%, and 10 wt% in DI water. During the measurement, a stainless steel parallel spindle (Ø 25 mm) rotated while the lower Peltier plate was stationary. The gap (500 µm) between parallel plates was filled with slurries, and the temperature was maintained at 25 °C.

The averaged thickness of the Cu film was measured using a table top four point probe (CDE ResMap 273) choosing 80 spots along the diameter of each wafer. The percentage ratio of the standard deviation of thickness relative to the averaged value was used to calculate the WIWNU [12–14]. A surface profile topography system (KLA-Tencor HRP-350) was used to measure the surface roughness and the Cu dishing on Si wafers. Results of the WIWNU, the surface roughness, and the Cu dishing were presented statistically.

3 Results and discussion

The comparison of WIWNU before and after CMP experiments in different slurries is shown in Fig. 1. The trend in the WIWNU after CMP is indicated by arrows. It is interesting to see that the WIWNU is reduced by 30% using the Y_2O_3 slurry. Using the commercial SiO_2 slurry, on the contrary, it shows an increase in the WIWNU by 48%. Meanwhile, the wafer polished using the Y_2O_3 slurry also has better surface quality. As shown in Fig. 2, wafers polished using the Y_2O_3 slurry have lower arithmetic averaged surface roughness than that polished with the SiO_2 slurry. To understand the effects of abrasives on WIWNU and surface roughness, frictional and rheological results are shown in Figs. 3 and 4, respectively. In Fig. 3, it is observed that the Y_2O_3 slurry has lower friction coefficient than the SiO_2 slurry. In Figs. 4(a) and 4(b), it is clear that the SiO_2 slurry with higher concentration has the larger slope in shear stress-shear rate plots. With the increase in SiO_2 concentration, the slurry becomes more viscous. Viscosity is directly related to the friction and mass transfer among fluid layers [15]. The change in slope of the shear stress-rate plots implies movement of one fluid layer respect to another with significant mass transfer. This is the evidence of a turbulent flow [16]. With the same concentration,

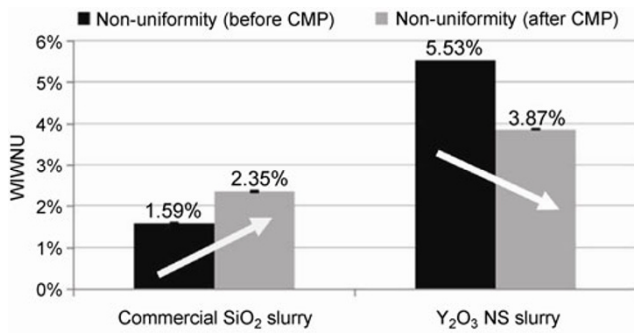


Fig. 1 Changes of WIWNU before (black) and after (gray) CMP using different slurries.

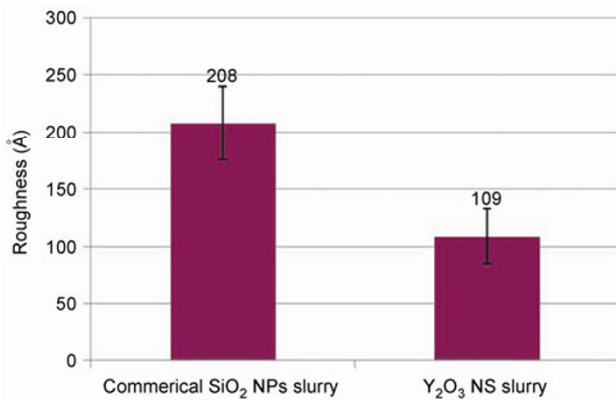


Fig. 2 The arithmetic averaged surface roughness of wafers that are polished using different slurries.

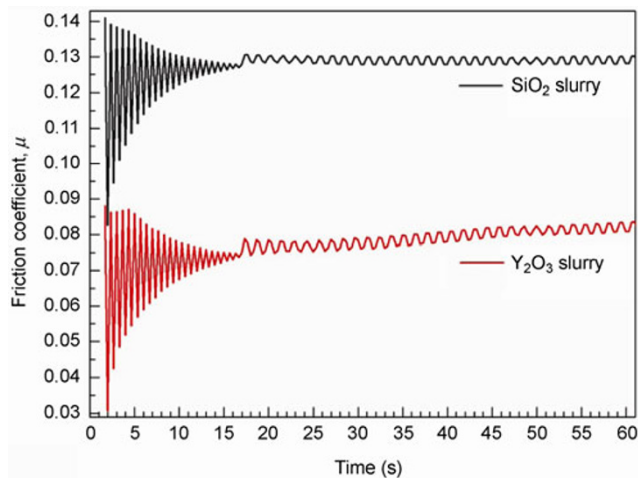


Fig. 3 Results of friction between the Cu film and the polishing pad in SiO₂ (black, top) and Y₂O₃ (red, bottom) slurries.

the shear stress in SiO₂ slurry changes at a faster rate against the shear rate than the Y₂O₃ slurry, as shown in Fig. 4(c). It is interesting to observe in Fig. 4(d) that the ratio of shear stress to shear rate in water is not

affected by the addition of Y₂O₃ NS. The unchanged slope of the shear stress-rate plots indicates the movement of one fluid layer past another with little matter transfer. This is the evidence of a laminar flow [17]. It is concluded from rheological measurements that SiO₂ NPs increases the viscosity of slurries while Y₂O₃ NS shows no effects.

Based on frictional behaviors and rheological properties of slurries, mechanisms in reduction of WIWNU are proposed in schemes illustrated in Fig. 5. When wafer is polished using the SiO₂ slurry, spherical NPs (see inset of Fig. 5(a)) can embed in the wafer and abrade it through particle-wafer contact mode (Fig. 5(a)) [18, 19]. Such abrasion through 3-body and 2-body wear is believed to be responsible for materials removal in CMP. On the contrary, when square Y₂O₃ NS (see inset of Fig. 5(b)) is used, it enables them to have larger contact area. The increased contact leads to a uniform distribution of the down force and the reduced contact pressure. When the applied pressure is low, a fluid film will be able to form between the pad and wafer (Fig. 5(b)) [20, 21]. As a result, the uniformed contact and improved slurry transport lead to more effective lubrication [22, 23]. This is confirmed by the friction results. Accordingly, polishing under lubricative condition can reduce the WIWNU after CMP [24]. In addition, when slurries entered the interface between the pad and wafer, Y₂O₃ NS can be deemed as parallel layers whereas SiO₂ NPs distribute chaotically and stochastically. As demonstrated by rheological experiments (Fig. 4), a laminar flow and a turbulent flow were believed to form in Y₂O₃ and SiO₂ slurries, respectively. A laminar slurry flow that has low viscosity with little flow fluctuation leads to uniform distributions of relative velocity and abrasive movement trajectories [5, 25]. In such the WIWNU is decreased.

In microelectronic devices, an important factor to planarize a wafer is elimination of Cu dishing [26, 27]. Results of Cu dishing in our CMP are shown in Fig. 6. Wafers polished with the Y₂O₃ slurry obtained less dishing than that polished with the SiO₂ slurry. During CMP, the protruded areas were polished while the low areas were passivated resulting in a smooth surface [18, 19]. Localized pad deformation occurs and has been reported to be an important reason causing metal

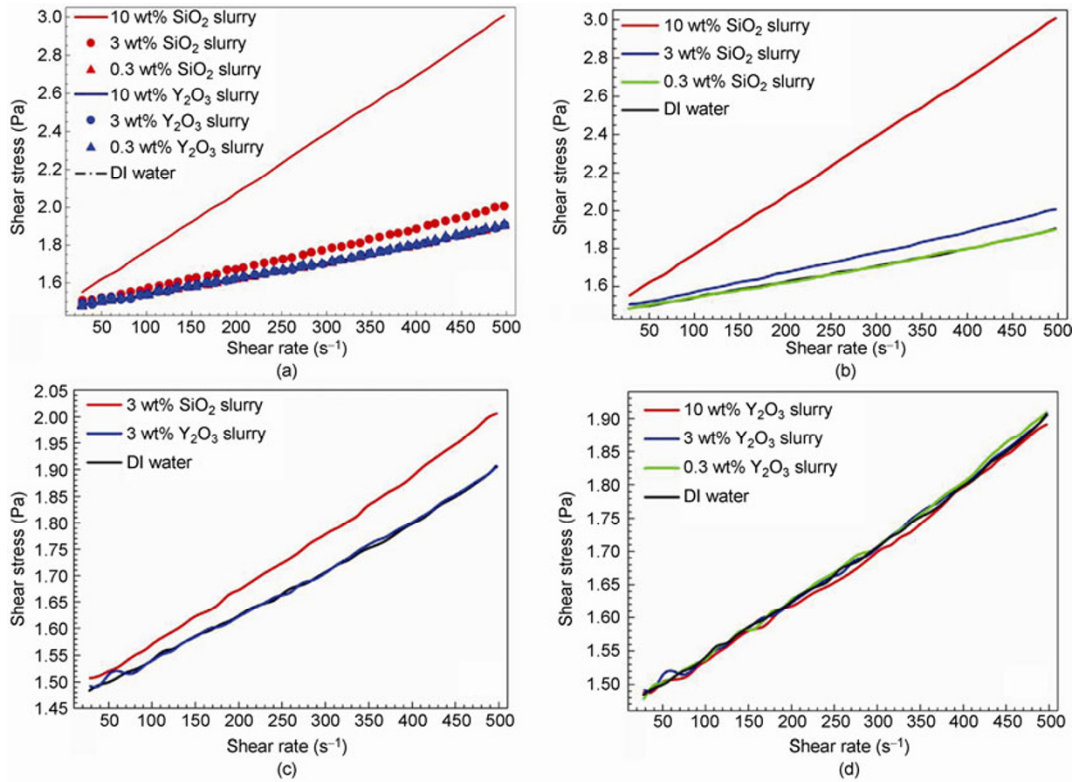


Fig. 4 Results of rheological measurements: (a) The comparison of shear stress-shear rate plots in different slurries with different abrasive concentrations; (b) variation of shear stress to shear rate in SiO₂ slurries with different concentrations; (c) the clear comparison of shear stress-shear rate plots in different slurries with the same abrasive concentration (3 wt%); (d) variation of shear stress to shear rate in Y₂O₃ slurries with different concentrations.

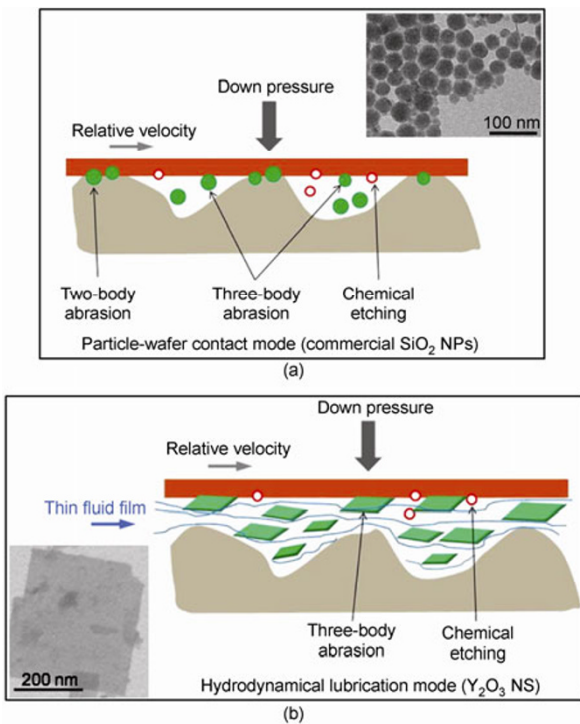


Fig. 5 Schematic representations of abrasion modes using the commercial SiO₂ NPs (inset) slurry (a) and the Y₂O₃ NS (inset) slurry (b).

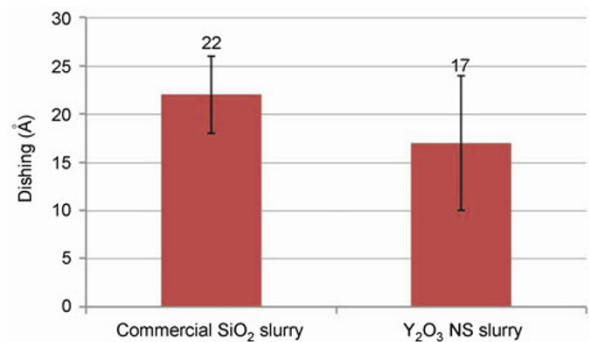


Fig. 6 The Cu dishing in wafers that are polished using different slurries.

dishing [26, 28, 29]. In the current work, however, Y₂O₃ NS has larger contact area than SiO₂ NPs. The down force distributes uniformly in the contact area. The low area undertakes a comparable pressure to that protruded area experiences. A uniform pressure distribution is beneficial for reduction in dishing [26]. In addition, dishing can be reduced through gentle contacts of pad through Y₂O₃ NS to wafer, which is similar to soft landing in abrasive free polishing [30–32].

The CMP conducted using the Y_2O_3 slurry obtained little dishing.

4 Conclusion

A new slurry containing Y_2O_3 NS was developed for CMP applications. Results showed that a slurry containing 3 wt% Y_2O_3 NS could reduce the WIWNU for 30% whereas the commercial SiO_2 slurry increased WIWNU for 48%. Low dishing (17 Å) was obtained using Y_2O_3 slurry comparing to that commercial SiO_2 slurry (22 Å). This is due to the fact that the sheet-shaped nanoparticles promote a uniform contact pressure distribution at the interface between a pad and wafer. These nanosheets are believed to increase the laminate flow resulting efficient slurry transport. The current study opens new approaches to develop slurries and is beneficial to optimize the manufacturing processes in microelectronics.

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Electronic Supplementary Material: The nano-sheet shape of Y_2O_3 NS which is shown with an Atomic force microscopy (AFM) image in Fig. S1 is available in the online version of this article at <http://dx.doi.org/10.1007/s40544-013-0017-z>.

References

- [1] Liang H, Craven D. *Tribology in Chemical-Mechanical Planarization*. Boca Raton (USA): CRC Press, 2005.
- [2] Ein-Eli Y, Starosvetsky D. Review on copper chemical-mechanical polishing (CMP) and post-CMP cleaning in ultra large system integrated (ULSI)—An electrochemical perspective. *Electrochim Acta* **52**: 1825–1838 (2007)
- [3] Zantye P B, Kumar A, Sikder A K. Chemical mechanical planarization for microelectronics applications. *Mater Sci Eng R Rep* **45**: 89–220 (2004)
- [4] Joo S, Liang H. Tribo-electrochemical characterization of copper with patterned geometry. *Microelectron Eng* **98**: 12–18 (2012)
- [5] Su J, Chen X, Du J, Guo D, Kang R. Analyzing on nonuniformity of material removal in silicon wafer cmp based on abrasive movement trajectories. *Adv Mater Res* **53–54**: 119–124 (2008)
- [6] Hocheng H, Tsai H Y, Tsai M S. Effects of kinematic variables on nonuniformity in chemical mechanical planarization. *Int J Mach Tool Manu* **40**: 1651–1669 (2000)
- [7] Feng T. Nonuniformity of wafer and pad in CMP: Kinematic aspects of view. *IEEE Trans Semicond Manuf* **20**: 451–463 (2007)
- [8] Kim H, Jeong H. Effect of process conditions on uniformity of velocity and wear distance of pad and wafer during chemical mechanical planarization. *J Electron Mater* **33**: 53–60 (2004)
- [9] Lee H, Park B, Jeong H. Influence of slurry components on uniformity in copper chemical mechanical planarization. *Microelectron Eng* **85**: 689–696 (2008)
- [10] Sikder A K, Giglio F, Wood J, Kumar A, Anthony M. Optimization of tribological properties of silicon dioxide during the chemical mechanical planarization process. *J Electron Mater* **30**: 1520–1526 (2001)
- [11] He X, Joo S, Xiao H, Liang H. Boron-based nanoparticles for chemical-mechanical polishing of copper films. *ECS J Solid State Sci Technol* **2**: P20–P25 (2013)
- [12] Kasai T, Bhushan B. Physics and tribology of chemical mechanical planarization. *J Phys: Condens Matter* **20**: 225011 (2008)
- [13] Chemali C E, Moyne J, Khan K, Nadeau R, Smith P, Colt J, Chapple-Sokol J. Multizone uniformity control of a chemical mechanical polishing process utilizing a pre- and postmeasurement strategy. *J Vac Sci Technol A* **18**: 1287–1296 (2000)
- [14] Tso P, Wang Y, Tsai M. A study of carrier motion on a dual-face CMP machine. *J Mater Process Technol* **116**: 194–200 (2001)
- [15] Ward-Smith J. *Mechanics of Fluids*, 9 Edition. New York (USA): CRC Press, 2011.
- [16] Taylor G. The dispersion of matter in turbulent flow through a pipe. *Proc R Soc Lond A* **223**: 446–468 (1954)
- [17] Spalding D B. Mass transfer in laminar flow. *Proc R Soc Lond A* **221**: 78–99 (1954)
- [18] Luo J, Dornfeld D A. Material removal mechanism in chemical mechanical polishing: Theory and modeling. *IEEE*

- Trans Semicond Manuf* **14**: 112–133 (2001)
- [19] Bozkaya D, Müftü S. A material removal model for cmp based on the contact mechanics of pad, abrasives, and wafer. *J Electrochem Soc* **156**: H890–H902 (2009)
- [20] Runnels S R, Eyman L M. Tribology analysis of chemical-mechanical polishing. *J Electrochem Soc* **141**: 1698–1701 (1994)
- [21] Chen J M, Fang Y-C. Hydrodynamic characteristics of the thin fluid film in chemical-mechanical polishing. *IEEE Trans Semicond Manuf* **15**: 39–44 (2002)
- [22] Liang H. Chemical boundary lubrication in chemical-mechanical planarization. *Tribol Int* **38**: 235–242 (2005)
- [23] Grover G S, Liang H, Ganeshkumar S, Fortino W. Effect of slurry viscosity modification on oxide and tungsten CMP. *Wear* **214**: 10–13 (1998)
- [24] Nolan L, Cadien K. Copper CMP: The relationship between polish rate uniformity and lubrication. *ECS J Solid State Sci Technol* **1**: P157–P163 (2012)
- [25] Lin S, Wu M. A study of the effects of polishing parameters on material removal rate and non-uniformity. *Int J Mach Tool Manu* **42**: 99–103 (2002)
- [26] Fu G, Chandra A. An analytical dishing and step height reduction model for chemical mechanical planarization (CMP). *IEEE Trans Semicond Manuf* **16**: 477–485 (2003)
- [27] Nguyen V H, Daamen R, van Kranenburg H, van der Velden P, Woerlee P H. A physical model for dishing during metal CMP. *J Electrochem Soc* **150**: G689–G693 (2003)
- [28] Vlassak J J. A contact-mechanics based model for dishing and erosion in chemical-mechanical polishing. *Mater Res Soc Symp* **671**: M4.6.1–M4.6.6 (2001)
- [29] Saka N, Lai J Y, Chun J H, Shu N P. Mechanisms of the chemical mechanical polishing (CMP) process in integrated circuit fabrication. *CIRP Ann Manuf Technol* **50**: 233–238 (2001)
- [30] Kondo S, Sakuma N, Homma Y, Goto Y, Ohashi N, Yamaguchi H, Owada N. Abrasive-free polishing for copper damascene interconnection. *J Electrochem Soc* **147**: 3907–3913 (2000)
- [31] Chiu J, Yu C, Shen S. Application of soft landing to the process control of chemical mechanical polishing. *Microelectron Eng* **65**: 345–356 (2003)
- [32] Denardis D, Sorooshian J, Habiro M, Rogers C, Philipossian A. Tribology and removal rate characteristics of abrasive-free slurries for copper CMP applications. *Jpn J Appl Phys* **42**: 6809–6814 (2003)



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