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Preparation of a novel catalyst ($SoFe^{III}$) and its catalytic performance towards the removal rate of sapphire substrate during CMP process

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ABSTRACT

Chemical mechanical polishing of sapphire with a novel catalyst ($SoFe^{III}$)-based colloidal silicon dioxide has been studied with high resolution transmission electron microscopy and X-ray diffraction. It has been found that a polytype of aluminun trihydroxide is formed on the polished crystal surface when $SoFe^{III}$-80 °C catalyst is used, while aluminum silicate hydrate layer is found on the polished sapphire surface when burnished with catalyst-free slurry. And the novel catalyst plays effective performance towards improving the removal rate of sapphire, and its removal rate is 7.21 μm/h, 1.66 times than the material removal rate obtained with catalyst-free slurry. Additionally, the optimum CMP removal by $SoFe^{III}$-80 °C yielded an ultra-smooth wafer surface with an average roughness of 0.0543 nm.

1. Introduction

Sapphire possesses excellent mechanical and optical properties, e.g. fantastic heat resistant, chemically inert and high hardness, has been broadly-utilized in a wide range of adhibitions, substrate for the heteroepitaxial growth of semiconductor material or microelectronic, precision anti-friction bearing, optics, electronics, solid laser, infrared window and other high-tech fields [1–6]. In all of these applications, the surface flatness of sapphire determines their performances. Its planarization method, undoubtedly, is crucially important. It is generally known that sapphire substrate is hard to be polished for its intrinsic nature (such as high hardness and inert chemical characteristic et al.). Substantial efforts have been devoted to get sapphire substrate with atomic-level smooth surface [7]. Up to now, chemical mechanical polishing (CMP), which involves removal of materials by a specific combination of chemical and mechanical action generating highly planar and ultra-smooth surface, is routinely used as the last planarization process to achieve atomic-level smooth wafer surface and is extensively accepted as global planarization technology in the semiconductor and sapphire substrates related manufacturing [7–12]. While in case of the CMP of sapphire substrate, there are two critical challenges, one of that is low removal rate of sapphire and the other is to figure out the mechanism of formation of the chemical reaction layer during the CMP process, although there are several approaches to this issue, most of them lie in the fact that sapphire CMP process is accompanied by a complicated chemical reaction between Al_2O_3 and colloidal silica (SiO_2) abrasive. Therefore, making clear of the CMP mechanism and improving planarization efficiency play a key role to fulfill the demand of higher surface quality.

In CMP, abrasive particles are one of the essential influencing factors. The species of abrasive and its hardness, size, distribution and dispersibility are important for a desired CMP performance. SiO_2 abrasives have been broadly used as polishing abrasive particles in CMP process [13–17]. And the average roughness (Ra) of sapphire polished with colloidal silica abrasive is lower than that polished with ceria, alumina, silicon carbide and any other abrasives under the same CMP conditions. However, the material remove rate (MRR) of sapphire polished with SiO_2 nanoparticles still needs to be improved. In order to achieve higher MRR value of sapphire and ultra-smooth surfaces, several active abrasives polishing higher polished surface quality such as magnesium oxide, ferric oxide and SiO_2-based modified abrasive particles, as well as compound particles have been studied [18–23]. All of them facilitated chemical reaction and/or mechanical removal during CMP process, while the removal rate of sapphire is still low. Our previous work firstly reported an effective Fe–Nx/C catalyst was synthesized to improve the MRR of

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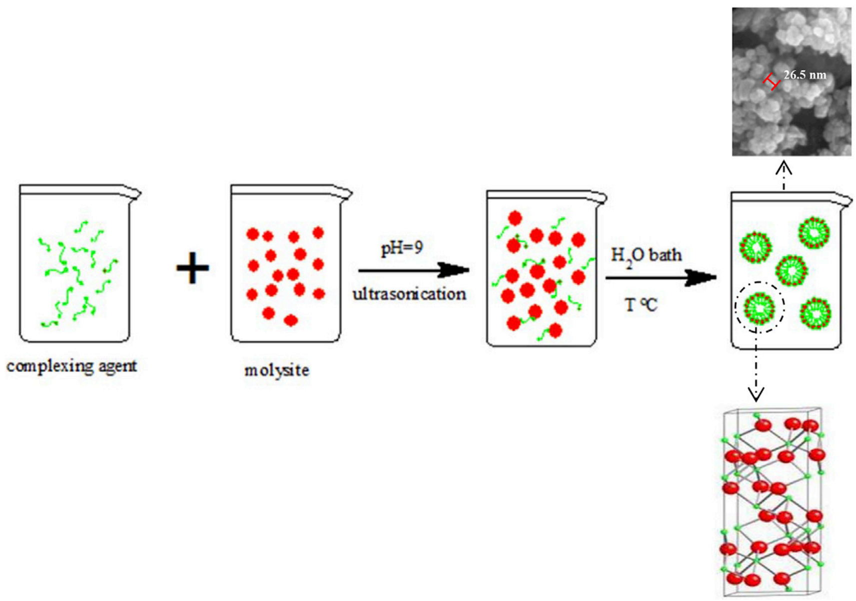

Fig. 1. Schematic presentation of the preparation of $SoFe^{III}$ catalyst.

sapphire in CMP process [24]. Based on this thoughtfulness, we developed a new ferrum-based catalyst ($SoFe^{III}$), and its CMP performances on sapphire wafer was studied in this work.

2. Experimental

2.1. Materials and preparation

Molysite (AR) and any other chemical reagents were purchased from Guoyao Co., Ltd. The $SoFe^{III}$ catalyst was synthesized through a simple method, the mechanism of $SoFe^{III}$ catalyst formation is described in Fig. 1. First, a total of 4 mmol complexing agent was dissolved in 30 mL distilled water, and then 40 mmol of molysite was added to the above mentioned solution. The mixture solution was keeping at pH = 9 by controlling the dropping speed of 1 M NaOH solution, and then after 60 min ultrasonic, the mixture solutions were kept in a H_2O bath for 18 h at desired temperature of 40 °C, 80 °C and 120 °C, respectively, to optimize catalytic activity.

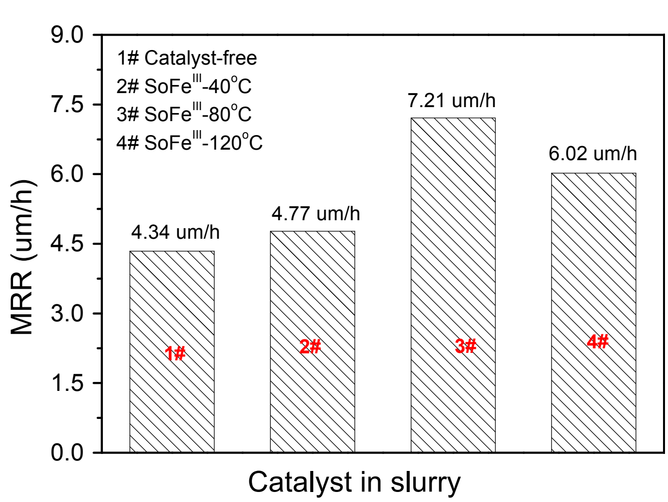

Fig. 2. Sapphire MRR with catalyst drying at different temperature.

2.2. Polishing process control and characterization methods

The catalyst-free-based SiO_2 slurry is a commercial source (Shenzhen Leaguer Material Co., Ltd). $SoFe^{III}$ nano-particles are used as catalyst and the pH is 9.0 for every slurry. All the polishing conditions and surface roughness characterization presented the same as we published before [24]. After planarization, all the sapphire wafers were cleaned by cleaner and distilled water, then blown out with clear nitrogen, and the MRR was calculated by mass loss as Eq. (1) [24],

$$MRR = \frac{\Delta m}{\rho S t} = \frac{\Delta m \times 10^6}{\rho \pi d^2 t} \quad (1)$$

Here:

Δm-the mass of sapphire before and after polishing, g;

d-radius of sapphire wafer, mm;

t-polishing time, h (in the test, t = 2/3 h);

ρ-density of sapphire substrate, g/cm^3 (3.98 g/cm^3);

A specific MRR is the average value of the removal rate of sapphire in three polishing operations under the same CMP conditions.

The crystal-phase of new born surface chemical product on wafer samples were detected by X-ray diffraction (XRD) with Cu Ka radiation and High Resolution Transmission Electron Microscopy (HRTEM).

3. Results and discussion

3.1. The CMP performance on sapphire in a catalytic slurry

Sapphire is a kind of super-hard-to process and inert material. In our previous work [24], for the sake of a higher MRR of sapphire during CMP process, catalytic agent Fe-Nx/C was exploited and then generated a soft hydration boehmite layer, which is much easier to be removed by SiO_2 abrasive particles during CMP process. While its removal mass was 2.3 μm/h, still not meet the demand of commercial utilization. Here, we synthesized a novel $SoFe^{III}$ catalyst to optimize the removal efficiency of sapphire. In order to get an optimal $SoFe^{III}$ catalyst, we mixed the commercial SiO_2 slurry with the $SoFe^{III}$ catalyst synthesized at different temperature as depicted previous. “40 °C” indicates the sample in a water bath at 40 °C and so on, as shown in Fig. 2. A larger MRR under a contained $SoFe^{III}$ slurry indicates that this novel catalyst plays a positive role