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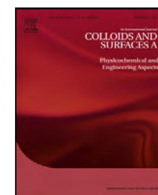

Role of amines and amino acids in enhancing the removal rates of undoped and P-doped polysilicon films during chemical mechanical polishing

P.R. Veera Dandu, B.C. Peethala, Naresh K. Penta, S.V. Babu*

Department of Chemical & Biomolecular Engineering, Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699, United States

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ABSTRACT

During chemical mechanical polishing, removal rates of undoped and P-doped polysilicon films as high as 200 and 250 nm/min, respectively, have been achieved using several abrasive-free solutions, each consisting of an amine or amino acid. It was observed that only α-amine(s) solutions enhance the removal rates of both undoped and P-doped polysilicon films. Potentiodynamic, zeta potential, contact angle, thermo gravimetric and EDS measurements were performed to examine the role of these α-amines in achieving high polysilicon removal rate. Possible removal mechanism of both undoped and P-doped polysilicon film in the presence and absence of the different additives is also proposed.

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1. Introduction

During the fabrication of microelectromechanical systems (MEMS) and integrated circuit devices, polysilicon has to be polished to planarize the surface in order to avoid the issues associated with depth of focus non-uniformity and photoresist step coverage, etc. [1,2]. Since the polysilicon layers are quite thick, exceeding several micrometers, especially in MEMS fabrication [1–5], they need to be polished at a high rate to maintain throughput. Several commercial slurries [3–10] containing various combinations of abrasives and additives have been developed to meet these requirements.

In several emerging applications [1,2,10], preferential removal of polysilicon over silicon dioxide and silicon nitride is required. We recently reported several silica- and ceria-based dispersions that enhanced the undoped polysilicon RRs to >500 nm/min in the presence of arginine and lysine HCl [8,9] and guanidine carbonate (GC) [10] at pH 9 and 10, while simultaneously suppressing silicon dioxide and silicon nitride RRs to <2 nm/min [8,9]. The silicon dioxide and silicon nitride RR behavior in the presence of these additives was discussed in our earlier publication [8], but not the polysilicon removal mechanism. Now, while investigating the polysilicon RR in the presence of large number of different amines and amino acids (Fig. 1), we identified several *abrasive-free* slurries which polish both undoped and P-doped polysilicon films at >200 and >250 nm/min, respectively, with ~0 nm/min dissolution rates.

The absence of abrasives and dissolution offer a compelling combination since they can facilitate planarization with minimal defect formation. Since the P-doped films (prepared with an implantation dose of $\sim 10^{15}$ ions/cm^2 at 80 keV for ~15 s) have adequate electrical conductivity, it was possible to perform several potentiodynamic measurements with them. Even though doping specifics like the level, type and depth of doping have a significant effect on polysilicon RRs [11–13], our focus here is only on the role played by the different additives, solution pH and doping (not its specifics) on the RRs.

Since our earlier results [8–10] showed that arginine, lysine and picolinic acid enhanced undoped polysilicon RRs in silica- and ceria-based dispersions at pH 10, we investigated a large number of amines and amino acids as potential additives. The different amines and amino acids investigated here are shown in Fig. 1. Several of these choices are based on the molecular structure of arginine, which can be considered to comprise of glycine and guanidine, and that of lysine to comprise of glycine and ethyl amine. We used GC since it is several orders of magnitude cheaper than guanidine. Interestingly, with 1 wt% glycine or GC abrasive-free solutions, the polysilicon (both doped and undoped) RRs were enhanced to >200 nm/min from >70 nm/min obtained with just pH adjusted water, while there was no increase in the case of 1 wt% ethyl amine abrasive-free solution, all at pH 10 (all as shown later in Fig. 2). Since

* Corresponding author.
E-mail address: babu@clarkson.edu (S.V. Babu).

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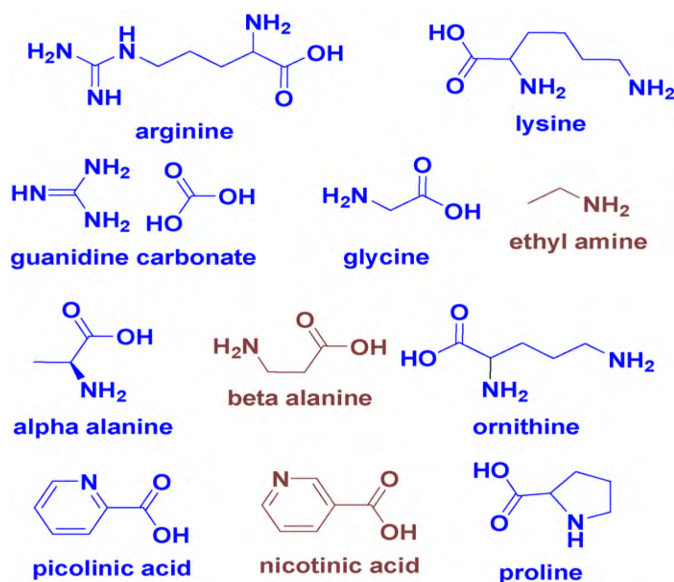

Fig. 1. Structures of different additives in the aqueous solutions used for polishing. Here, all these additives contain α-amine(s) except ethyl amine, β-alanine and nicotinic acid.

the >200 nm/min RRs are quite useful and interesting, the remainder of this paper deals only with the use of abrasive-free aqueous solutions for polishing. The common functional group in guanidine, glycine, arginine and lysine is the α-amino group(s), suggesting the possibility that the α-amino group might be responsible for the RR enhancement.

The importance of the α-amino group is indeed validated when the RRs of both the undoped and P-doped polysilicon films with several other α-amine(s) containing compounds (α-alanine, ornithine, glycine and proline) were measured. They are all about the same but more important all are higher compared to those obtained with solutions of ethyl amine, nicotinic acid and β-alanine, all of which lack the α-amino groups. In all the investigated cases, undoped polysilicon film RRs obtained were slightly lower than that of the P-doped polysilicon RRs. Potentiodynamic, zeta potential, thermogravimetric, energy dispersion spectroscopy (EDS) and contact angle measurements were performed with either the doped polysilicon films or polysilicon powder to examine the role of the α-amino groups. We propose a possible mechanism for the observed polysilicon RR changes due to the phosphorous impurities in the film and the additive binding on the polysilicon surface.

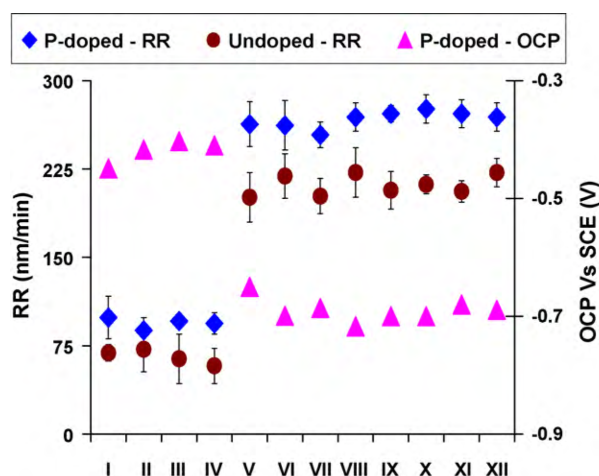

Fig. 2. RRs and OCP values of polysilicon with different additives (1 wt%) at pH 10: (I) no additive (II) ethylamine (III) β-alanine (IV) nicotinic acid (V) picolinic acid (VI) α-alanine (VII) guanidine carbonate (VIII) arginine (IX) lysine (X) ornithine (XI) glycine and (XII) proline. Here II–IV are non-α-amines and the rest are α-amines.

2. Materials

Phosphorous doped (with a dosage of ~10^{15} ions/cm^2 at 80 keV for ~15 s) polysilicon (LPCVD, at ~550 °C) wafers, with an initial thickness of ~150 nm of polysilicon, with an intervening layer ~30 nm thick silicon nitride between the polysilicon film and the Si substrate, were supplied by IBM, Albany. The undoped polysilicon (LPCVD, at ~610 °C) wafers with an initial thickness of ~2000 nm of polysilicon with an intervening layer ~150 nm thick silicon dioxide were supplied by Montco Silicon Technologies. Both these wafers were cut into 1 in. × 1 in. square coupons, mounted at the center of an 8 in. silicon dioxide wafer using a double-sided tape and were polished on a G&P polisher using aqueous solutions containing the 12 amines and amino acids shown in Fig. 1. Polysilicon (d_m ~270 nm) powder was used to perform zeta potential, TGA and EDS measurements. All the chemical reagents and polysilicon powder were obtained from Sigma–Aldrich and used as supplied.

3. Experimental techniques

Chemical mechanical polishing: The polishing conditions were typically 4/5.5 psi operating/retaining ring pressure, 75/75 rpm carrier/platen rotation, slurry flow rate of ~200 ml/min and a polish time of 25 s. This short polishing time was necessary since for larger times in several cases the 150 nm thick P-doped polysilicon film was entirely removed due to its high RR. The polishing pad (IC1000) was conditioned *in situ* using a diamond-grit pad conditioner supplied by 3 M. The polish results shown are an average of the RRs from two polished wafer coupons. The removal rate was calculated from the difference in film thickness before and after polishing measured at nine points, using a Filmetrics F20 interferometer.

Zeta potentials: Zeta potential values of 1 wt% polysilicon (d_{mean} ~270 nm) suspensions were measured in the presence and absence of different additives at pH 10, using a Matec Applied Science Model 9800 Electro acoustic analyzer. Polysilicon particles were used to represent the surface of the polysilicon film being polished. The samples were titrated with KOH or HNO_3 to vary the pH.

Potentiodynamic measurements: The potentiodynamic experiments were performed using a Gamry PCI4 G-300 series potentiostat. A standard calomel electrode (SCE) and platinum wire were used as reference and counter electrodes, respectively. Doped polysilicon wafer coupons (2 × 2 cm^2) were used as the working electrode. A fresh wafer coupon was used for each electrochemical experiment. The coupons were electrically connected to the potentiostat by a copper alligator clip. All the solutions contained 0.05 M KNO_3 to ensure adequate conductivity and were prepared using deionized water and reagent grade chemicals, and KOH/HNO_3 was used as pH adjusting agents. The voltage was scanned at a rate of 5 mV/s in the range of ±0.5 V around open circuit potential (OCP) for potentiodynamic measurements. Corrosion current (I_{corr}) was obtained from the Tafel plots where the anodic and cathodic current branches meet [14–16]. Corrosion potential and open circuit potential values obtained with all the aqueous solutions investigated here are almost the same.

Sample preparation for thermogravimetric analysis (TGA) and EDS: Several samples (each 200 ml) were prepared by first dissolving different additives in a sufficient amount of deionized water to reach 1 wt% concentration and adjusted to pH 10, followed by the addition of 1 wt% polysilicon (d_m ~270 nm) powder and stirred well for 30 min. Each of these dispersed samples was centrifuged and

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