ELSEVIER

Microelectronics Journal 37 (2006) 519–525

Microelectronics
Journal

www.elsevier.com/locate/mejo

Etch characteristics of KOH, TMAH and dual doped TMAH for bulk micromachining of silicon

K. Biswas*, S. Kal

Microelectronics Laboratory, Advanced Technology Centre/E & ECE Department, Indian Institute of Technology, Kharagpur 721302, India

Received 20 May 2005; received in revised form 25 July 2005; accepted 27 July 2005

Abstract

High precision bulk micromachining of silicon is a key process step to shape spatial structures for fabricating different type of microsensors and microactuators. A series of etching experiments have been carried out using KOH, TMAH and dual doped TMAH at different etchant concentrations and temperatures wherein silicon, silicon dioxide and aluminum etch rates together with <100> silicon surface morphology and <111>/<100> etch rate ratio have been investigated in each etchant. A comparative study of the etch rates and etched silicon surface roughness at different etching ambient is also presented.

From the experimental studies, it is found that etch rates vary with variation of etching ambient. The concentrations that maximize silicon etch rate is 3% for TMAH and 22 wt.% for KOH. Aluminum etch rate is high in KOH and undoped TMAH but negligible in dual doped TMAH. Silicon dioxide etch rate is higher in KOH than in TMAH and dual doped TMAH solutions. The <111>/<100> etch rate ratio is highest in TMAH compared to the other two etchants whereas smoothest etched silicon surface is achieved using dual doped TMAH. The study reveals that dual doped TMAH solution is a very attractive CMOS compatible silicon etchant for commercial MEMS fabrication which has superior characteristics compared to other silicon etchants.

Keywords: MEMS; Bulk micromachining; KOH; TMAH; Dual doped TMAH; Surface roughness; <111>/<100> Etch rate ratio

1. Introduction

Bulk silicon micromachining is an essential process step for the fabrication of MEMS devices. Anisotropic wet chemical etching of silicon is frequently used for shaping quite intricate three-dimensional structures such as proof masses, cantilevers, diaphragms, trenches and nozzles on silicon substrate [1]. Presently, dry etching techniques (RIE and DRIE) are employed for high aspect ratio silicon micromachining but wet chemical etching still dominates over dry etching due to its low process cost, simple etch setup, higher etch rate, better surface smoothness, high degree of anisotropy and lower environmental pollution. The study of silicon, silicon dioxide, aluminum etch rates along with topology of the etched silicon surface for various silicon etchants at different temperatures is necessary to develop a CMOS compatible commercial process for fabricating micromechanical devices. Compatibility of MEMS fabrication process with commercial IC fabrication technology allows for integration of microtransducers with integrated circuits which provides on-chip signal conditioning, interface control and remote signal transmission. The commonly used silicon etchants are classified into three main groups: (i) Alkali metal hydroxides [1–3] (ii) Diamines based [4] and (iii) Quaternary ammonium hydroxides [5,6]. KOH (potassium hydroxide) is a non-toxic, economical and commonly used alkali metal hydroxide silicon etchant which requires simple etch setup and provides high silicon etch rate, high degree of anisotropy, moderate Si/SiO_2 etch rate ratio and low etched surface roughness [2,3]. But KOH damages exposed aluminum metal lines very quickly and is not CMOS compatible due to the presence of alkali metal ions in it. EDP (ethylenediamene pyrocatecol) is a diamine based silicon etchant which has moderate silicon etch rate, high Si/SiO_2 etch rate ratio, low degree of anisotropy and is partly CMOS compatible [4]. But EDP ages quickly,

---

* Corresponding author. Tel.: +91 3222 281479; fax: +91 3222 255303.
E-mail address: kanishka@ece.iitkgp.ernet.in (K. Biswas).

0026-2692/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mejo.2005.07.012

requires a complex etching apparatus and careful handling as it produces reaction gases which are health hazardous and so require special safety measures. TMAH (tetramethyl ammonium hydroxide) is the most preferred quaternary ammonium hydroxide based silicon etchant [5,6]. TMAH is gaining popularity despite its high cost and complex etch setup because it is a non-toxic, CMOS compatible organic solution which has moderately high silicon etch rate and high selectivity to masking layers. Ordinary TMAH yields rough etched silicon surfaces but when TMAH is doped with suitable amounts of silicic acid and AP (ammonium peroxodisulphate, $(NH_4)_2S_2O_8$), the mixture provides complete aluminum passivation along with smooth etched surfaces [7–9].

In the present investigation, studies have been made on (i) silicon etch rate, (ii) <111>/<100> etch rate (ER) ratio and (iii) etched <100> silicon surface roughness using KOH, TMAH and dual doped TMAH solutions. The etching experiments were performed using different KOH (10, 22, 33 and 44 wt.%) and TMAH (3, 8, 12 and 20%) solution concentrations and at different bath temperatures (50 to 80 °C). The dual doped TMAH etching experiments were carried out using 2 and 5% TMAH solution. Our earlier study [9] reported that 2% TMAH doped with 30 gm/l silicic acid and 5 gm/l of AP whereas 5% TMAH doped with 38 gm/l silicic acid and 7 gm/l AP provides high silicon etch rate, smooth etched silicon surface and almost complete passivation of the exposed overlaying aluminum metal interconnection lines. This paper reports the experimental results and a comparison of the silicon etch rates, <111>/<100> ER ratio and etched silicon surface roughness for different Si-etchants, namely KOH, TMAH and dual doped TMAH solution.

2. Experimental

Both p-type (resistivity 10–40 Ω-cm) and n-type (resistivity 4–6 Ω-cm) single crystal <100> silicon substrates of diameter 4-inch and thickness 525 μm, were used for studying anisotropic etching of silicon in different etchants. Initially, a silicon dioxide layer of thickness around 1 μm was thermally grown by cyclic oxidation process. Rectangular and square oxide windows of suitable dimensions were opened at the front side of the wafer by photolithography process. Thereafter a 0.8 μm thick aluminum layer was deposited by thermal evaporation technique and photolithographically patterned. Before insertion of the samples in etching solution, native oxide was removed without damaging the aluminum metal patterns using a special native oxide etchant followed by rinsing in de-ionized water. Each set of experiment was repeated twice using two samples held vertically in the etching solution during etching. Etching at a particular ambient was carried out for a span of 30 min wherein the second sample was inserted 15 min after the first sample. The silicon and aluminum etch rates and etched surface roughness were measured by Dektak^3 surface profilometer by averaging the readings obtained from the *x*- and *y*-scans. The silicon dioxide thickness was measured using an ellipsometer. The <111>/<100> ER ratio were determined using an optical microscope and SEM.

2.1. Experiments using KOH-water solution

The KOH-water solution was prepared by diluting commercially available KOH pellets (84% pure, E.Merck, India). All experiments were carried out in a closed glass beaker with a constant temperature bath. No external mechanical stirring or reflex condenser was used in etch bath of KOH during experiments. KOH etching was performed using both p-type and n-type silicon substrates. The KOH concentration was varied from 10 to 44 wt.% and temperature of the etch bath from 50 to 80 °C in steps of 10 °C. The silicon dioxide etch rate was determined after 60 min of etching in KOH.

2.2. Experiments using ordinary TMAH-water solution

The TMAH-water solution was prepared by diluting commercially available TMAH (25 wt.%, Merck, Germany). All experiments were carried out in a closed glass vessel with a constant temperature bath. A water cooled reflex condenser was used to prevent changes in etchant concentration during etching. A magnetic stirrer rotating with speed of 100 rpm was used constantly during etching to facilitate uniform etching. The TMAH etching experiments were carried out using 3 to 20% TMAH at different bath temperatures (50 to 80 °C). An etching time of 120 min was used to determine silicon dioxide etch rate in TMAH.

2.3. Experiments using dual doped TMAH solution

For this study, 2 and 5% TMAH doped with silicic acid and AP was used at 60, 70 and 80 °C. The 2% TMAH solution was mixed with 30 gm/l silicic acid and 5 gm/l of AP whereas the 5% TMAH solution contained 38 gm/l of silicic acid and 7 gm/l AP [9]. During etching mechanical agitation was provided continuously with the help of a magnetic stirrer rotating at 100 rpm and a water cooled reflex condenser prevented any change of etchant concentration. The variation of aluminum, silicon and silicon dioxide etch rates were measured in each case. The silicon surface roughness measurements were also carried out.

3. Results and discussions

3.1. KOH solution

Fig. 1 shows the variation of the etch rates of n-type and p-type silicon for four different KOH concentrations at different bath temperatures. In the present study, 22 wt.% KOH solution provides maximum silicon etch rates of 89.2 and 88.1 µm/h for n-type and p-type silicon respectively at 80 °C. The dopant type of silicon substrate has little effect on the etch rate of silicon although n-type etches slightly faster than p-type silicon. Fig. 2 shows the variation of SiO_2 and Al etch rates at different temperatures and KOH concentrations. The silicon dioxide etch rate increases continuously with increase in temperature irrespective of KOH solution concentration. The maximum silicon dioxide etch rate is 450 nm/h at 80 °C using 33 wt.% KOH. The Al etch rate is appreciable in all KOH concentrations with maximum etch rate of 3.0 µm/min. The etched silicon surface smoothens with both increase in KOH concentration and bath temperature. Silicon surface roughness degrades with increase in etch duration due to the masking of hydrogen bubbles evolved during etching which significantly contributes to surface roughness [10–13]. Fig. 3(a) shows the SEM micrograph of p-type silicon surface etched in 22 wt.% KOH at 70 °C. The maximum silicon roughness value is 0.83 µm resulting from 10 wt.% KOH at 50 °C and the smoothest silicon surface has roughness value of 0.12 µm rough which is obtained using 33 wt.% KOH.

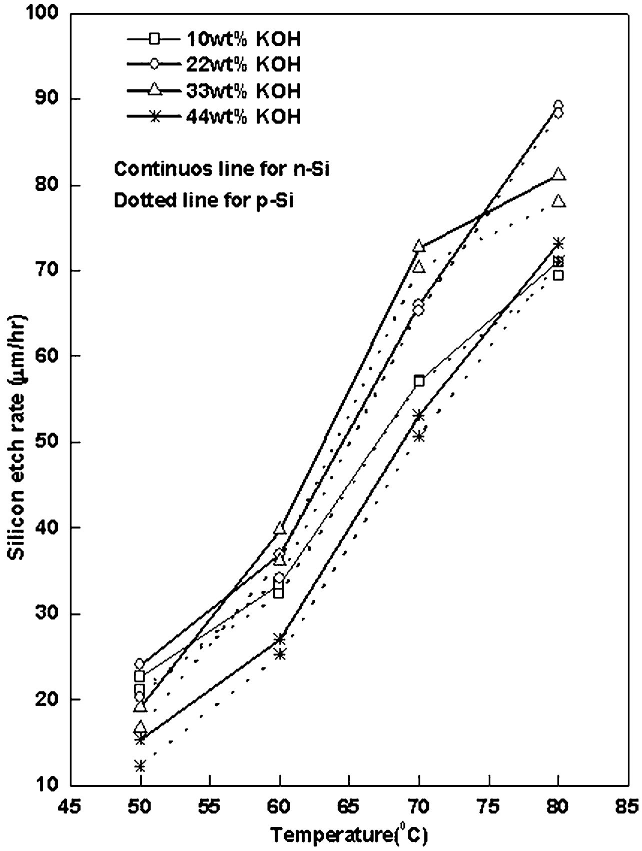

Fig. 1. Variation of the silicon etch rate with KOH concentration.

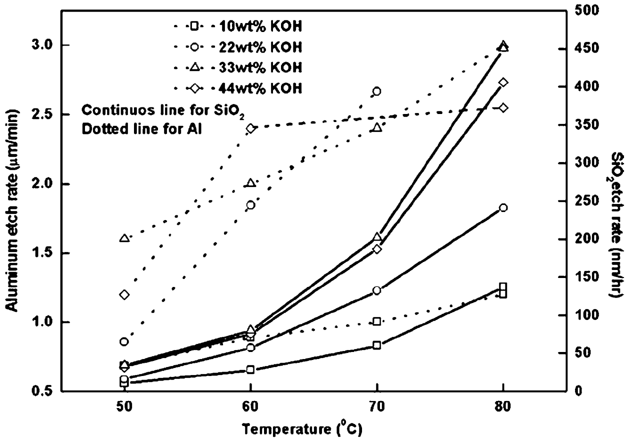

Fig. 2. Variation of the silicon dioxide and aluminum etch rates with KOH concentration.

3.2. TMAH solution

Fig. 4 shows the variation of the silicon etch rates with TMAH solution. The maximum silicon etch rate obtained is 60.2 µm/h using 3% TMAH at 80 °C. The silicon etch rate decreases with increase in TMAH concentration. Similar to KOH, dopant type of silicon substrate type has negligible effect on silicon etch rate. The silicon dioxide and Al etch rate for various TMAH concentrations is shown in Fig. 5. The silicon dioxide etch rate increases with both increase in temperature and decrease in TMAH concentration. The maximum silicon dioxide etch rate value is almost half in TMAH compared to KOH which is an attractive feature of TMAH. Undoped TMAH solution attacks aluminum film but to a less extent than KOH. The maximum aluminum etch rate is 1.44 µm/min in 20% TMAH at 80 °C. The etched silicon surface smoothness increases with both increase in TMAH concentration and temperature. The random pyramidal hillocks formed during etching significantly contributes to the surface roughness than other factors [11,14–16]. Fig. 3(b) shows the SEM micrographs of the etched silicon surface at TMAH concentration of 5% at 70 °C. The inset SEM photograph of Fig. 3(b) shows the random hillock formation on the etched silicon surface after 2 hours of etching in 3% TMAH at 50 °C. The maximum and minimum silicon roughness values are 3.7 and 0.04 µm which are obtained using 3% TMAH and 20% TMAH, respectively.

3.3. Dual doped TMAH solution

The variation of the etch rates of silicon, aluminum and silicon dioxide is presented in Fig. 6. The etch rate of silicon

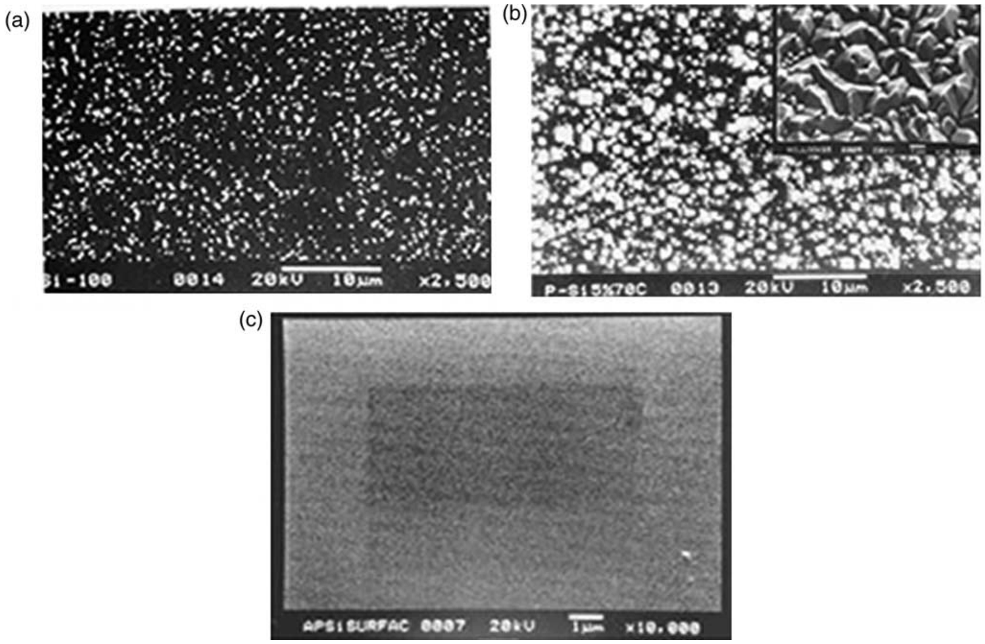

Fig. 3. SEM microphotograph of silicon<100> after etching in (a) 22 wt.% KOH at 70 °C (b) 8% TMAH at 70 °C (Inset: Hillock formation at low concentrations of TMAH) and (c) 5% dual doped TMAH at 80 °C [9].

in dual doped TMAH is almost comparable to that of KOH and TMAH but the masking silicon dioxide and aluminum etch rates are quite small which is desirable for MEMS fabrication technology. Dual doped TMAH also improves surface smoothness of the etched surfaces due to the suppression of random hillock formation by the oxidizing agent AP. The silicon surface roughness is three orders less in dual doped TMAH solutions in comparison to KOH and TMAH. Fig. 3(c) shows the SEM micrograph of the n-type silicon surface etched in 5% dual doped TMAH at 80 °C [9].

3.4. Comparative study

A comparative study of the etching characteristics of silicon, silicon dioxide and aluminum using three anisotropic silicon etchants (KOH, TMAH and dual doped TMAH) has been made. Fig. 7 silicon shows the comparison of the silicon etch rates for the three etchants whereas Fig. 8 presents the comparison of aluminum and silicon dioxide etch rates. The etched silicon < 100> surface roughness values for all the etchant concentrations are compared in Fig. 9. An analysis of

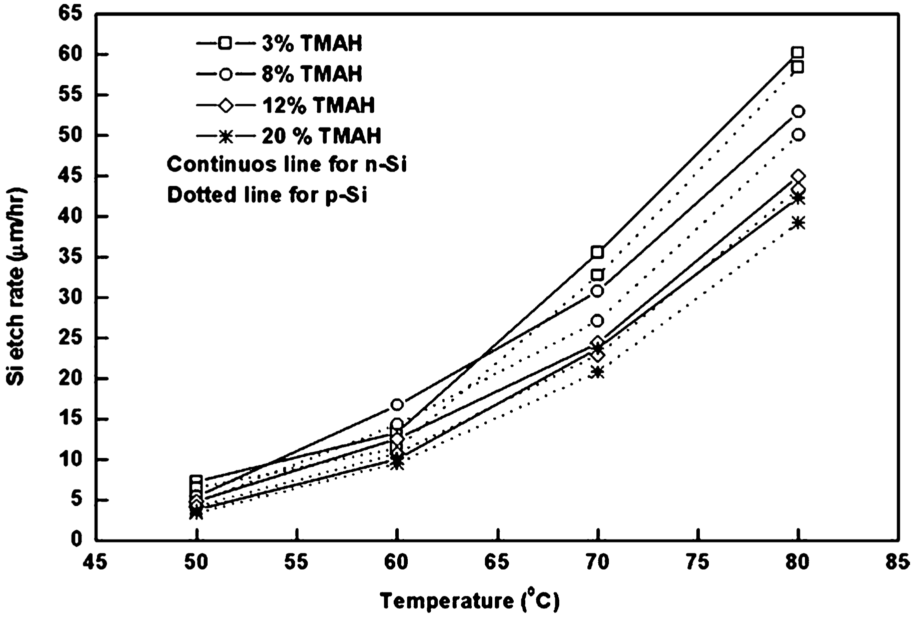

Fig. 4. Variation of the silicon etch rates with TMAH concentration.

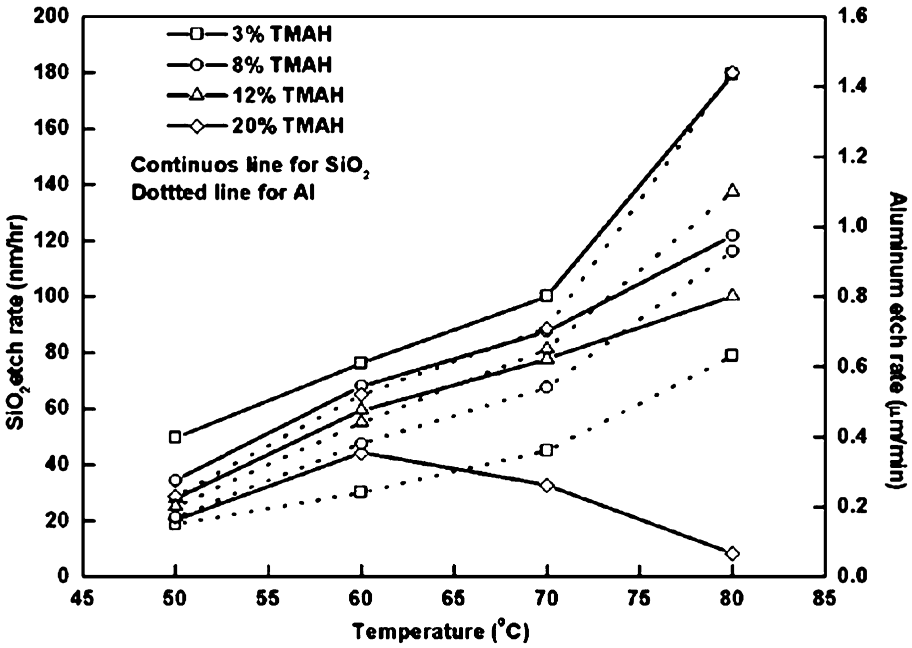

Fig. 5. Variation of the silicon dioxide and aluminum etch rates with TMAH concentration.

the comparison of the etch characteristics (Figs. 7–9) reveals that (a) the highest silicon etch rate is obtained using KOH solution at 80°C whereas dual doped TMAH solution provides complete aluminium passivation, (b) the silicon dioxide etch rate is approximately two times higher in KOH solutions compared to ordinary TMAH and three orders higher than dual doped TMAH solutions, (c) surface roughness of silicon etched in KOH solution is one order less compared to surfaces etched in undoped TMAH solution and (d) the etched silicon surface roughness is almost three orders less in dual doped TMAH compared to the other two etchants. The method used for determining the ER ratios of the etchants is shown in Fig. 10. The <111> etch rate was determined using SEM microphotographs. Fig. 11 presents the comparison of <111>/<100> ER ratios of the etchants. The <111>/<100> ER ratio was 1.68% for KOH, 3.44% for TMAH, 2.48 and 2.83% for 2 and 5% dual doped TMAH, respectively. The results

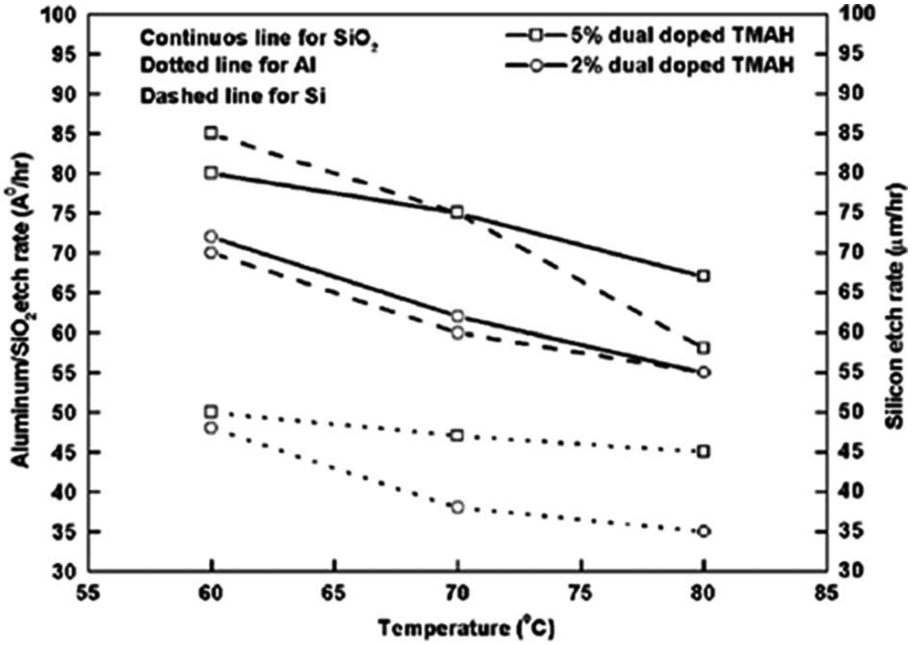

Fig. 6. Variation of the silicon, aluminum and silicon dioxide etch rates with dual doped TMAH.

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.

WHAT WILL YOU BUILD? | **sales@docketalarm.com** | **1-866-77-FASTCASE**