Green Semiconductor Manufacturing – Potential New Routes Using Aqueous Solution Chemistry

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Abstract

There are exceptional opportunities to increase materials efficiencies in semiconductor manufacturing. The challenge is maintaining or increasing performance while reducing waste. The Center for Green Materials Chemistry is developing a platform of solution based inks for direct deposition of high performance inorganic films at atmospheric pressure and low temperature. This platform should be useful for applications ranging from the extreme end of the nanoscale in support of wafer processing to state of the art large area substrates. Results are presented on the deposition of nanoscale thin films of high performance, fully dense amorphous materials from aqueous based solutions. Results are also presented demonstrating that these films can be directly patterned, eliminating the need for a separate photo resist layer.

INTRODUCTION

Semiconductor manufacturing as currently practiced is inherently an inefficient process. Typically wafers are blanket coated with an active layer that needs to be patterned. The active layer is coated with a photo resist layer (or combination of layers), which is then exposed and developed. The active layer is then etched away through the openings in the photo resist layer. Finally the photo resist layer (or layers) is removed. Of the material deposited on the wafer, only a small fraction of the active layer may remain and the photo resist layer (or layers) is completely removed after patterning. The waste in this subtractive processing, including the polymer resist, is directly proportional to the number of layers required to complete the desired chip, and this number continues to climb as more complex circuits in a smaller two dimensional area require more back end layers to connect the active components together in the desired circuit. Concurrent with the decrease in critical dimensions of devices, new materials are being introduced and more complex architectures are being created, leading to new challenges in processing.

Materials utilization becomes even worse if the layers are deposited via sputtering, CVD or physical evaporation in vacuum, as typically only a small fraction of the material delivered from the source actually deposits on the substrate. The extensive high cost capital equipment used to deposit these films results in semiconductor fabrication plants costing in the billons of dollars. Fabrication plants also consume large quantities of energy, as vacuums and high processing temperatures are energy intensive.

The "holy grail" to overcome materials inefficiencies is an additive processing technology where low processing temperatures and non-vacuum deposition technologies would also significantly reduce energy use during fabrication. Partial steps towards the goal of greater materials efficiency include the ability to directly pattern active materials without a separate photo resist. The advantages of direct printing have, of course, been recognized and several companies are based on the inherent advantages of additive processing. Early commercialization of this approach centered around "printing" with organics and several companies, such as PlasticLogic with its Que eReader (www.plasticlogic.com) and Konarka with organic photovoltaics (www.konarka.com) have demonstrated the feasibility of creating working devices with these materials. The issue with organic materials, however, is their inherent low performance due to the low mobility of conducting polymers, limiting their more general application. The higher performance of inorganic systems, combined with discoveries in the last decade in nanoscience, has resulted in the first generation of companies based on printing with inorganic nanoparticles. Kovio produces RFID tags with Si nanoparticle ink (www.kovio.com) and Nanosolar (www.nanosolar.com) is producing high performance copper indium gallium diselenide (CIGS) solar cells using nanoparticle inks in a proprietary process. Issues with inorganic "printing" based on nanoparticles include the intensive solution processing required to produce the nanoparticle inks, which uses significant energy and produces considerable chemical waste. High temperatures are also required to sinter the nanoparticles into a highly linked film to achieve high performance.

CENTER FOR GREEN MATERIALS CHEMISTRY

The technical goal of this National Science Foundation supported center is to develop a platform of solution-based

inks (no particles) for direct deposition of high-performance inorganic films at atmospheric pressure and low temperatures. The educational goal is to produce graduates with hands-on experience in semiconductor processing and trained in solving problems using inherently more efficient processes. As we illustrate below, the inorganic inks developed to date have been shown to form fully dense amorphous films that have been used as dielectrics in transparent thin film transistors. These active films can be directly patterned, taking advantage of solubility difference induced through condensation reactions triggered with small molecules such as peroxide or through interdiffusion of nanocomposite layers. This growing platform of solution-based inks (true solutions rather than nanoparticles or colloids) for direct deposition of high-performance inorganic films at atmospheric pressure and low temperatures has potential uses in applications ranging from the extreme end of the nanoscale in support of wafer processing to state-of-the-art large-area electronics and optoelectronics.

DENSE AMORPHOUS FILMS FROM AQUEOUS SOLUTIONS

The solution based synthesis of high quality solution based insulators has been a major obstacle to the development of useful all inorganic devices. Smooth, dense, and pinhole-free films are not typically obtained using sol-gel and related approaches, which rely on metal-organic precursors requiring controlled hydrolysis in combination with stabilizing ligands and organic solvents. Films prepared using this common approach suffer from disruptive volume loss, as high temperatures are used to decompose and drive off the organic components, leading to discontinuities, surface roughness, and crystallization.

An orthogonal approach has been taken by center researchers fostering native M-$(OH)_n$-M interactions within an aqueous precursor solution by controlling pH, limiting high volume ligands and non-functional counter ions, and preventing the formation of sol particles.[1] The metastable hydroxo frameworks [2] allow smooth hydrated films to rapidly dehydrate through a series of condensation reactions to yield glassy, fully dense films without cracking or pore formation as shown in Figure 1 for a gallium oxide film. Similar films have been prepared for a variety of oxides, including TiO_2, ZrO_2, HfO_2, Y:ZrO_2, Y:HfO_2, Ca:ZrO_2, $ZrSO_x$, $HfSO_x$ $ZrPO_x$, $HfPO_x$, V_2O_5, Nb_2O_5, Ta_2O_5, Fe_2O_3, ZnO, Al_2O_3, $InGaO_x$, $ZnInGaO_x$, $CuInGaO_x$ and La:$ZrSO_x$. The flexibility of this synthesis approach permits numerous inorganic oxides, with their wide band gaps, useful polarizabilities and chemical stabilities, to be used as insulators and dielectrics in devices. The techniques have also recently been extended to the synthesis of compound semiconductors such as $CuInS_2$ and $CuInSe_2$.

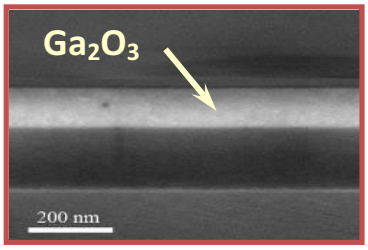


Figure 1: A fully dense amorphous Ga_2O_3 film prepared from an aqueous precursor solution.

NANOLAMINATES

The ability to form smooth, fully dense amorphous films by spin coating from aqueous solution enables nanolaminates, such as the $HfO_{2-x}(SO_4)_x/ZrO_{2-x}(SO_4)_x$ nanolaminate shown in Figure 2, to be prepared by alternative deposition of the constituents.[3] The ability to prepare these nanolamintes allows for the design and fabrication of optical devices based on variations in the optical absorbance. This ability also permits more complex oxides to be prepared from several solutions each containing only a single cation, thus overcoming issues of mutual solubility and the challenges inherent in trying to co-precipitate multiple cations from the same solution while maintaining the ratio of the components. These nanolaminate structures permit the diffusion lengths to be controlled via the period of the structure and the interdiffusion coefficients to be controlled using the relative

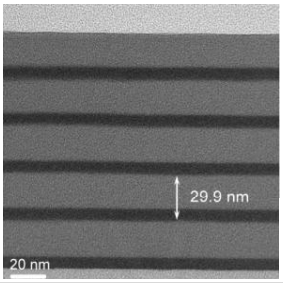


Figure 2: An SEM image of a $HfO_{2-x}(SO_4)_x/ZrO_{2-x}(SO_4)_x$ nanolaminate prepared by alternately coating each constituent from an aqueous solution.

hydration level of the layers. While center researchers are still exploring the evolution of nanolamintes as a function of temperature, hydration level and time, the preparation of an optical notch filter using this approach has already been demonstrated.

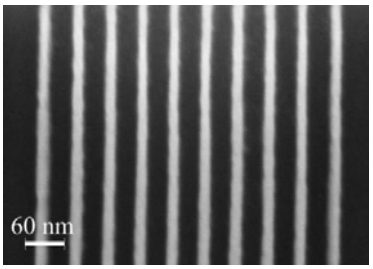
HIGH PERFORMANCE THIN FILMS

The fully dense films prepared from aqueous solutions have been tested as dielectrics by preparing metal-insulator-metal capacitors. [3,4] As an example of this process, 150 to 300nm thick films of $HfO_{2-x}(SO_4)_x$, $ZrO_{2-x}(SO_4)_x$ as well as films doped with La and Ca were spin coated onto Ta metal films that had been deposited on SiO_2 coated Si wafers. Arrays of 1.1-mm Al dots were deposited directly on the spin coated films. Breakdown fields of 3.5-6 $MVcm^{-1}$ were demonstrated with leakage currents of less than 50 $nAcm^{-2}$ at

fields of 1 $MVcm^{-1}$ for all films, with many films having leakage currents less than 10 $nAcm^{-2}$. Relative permittivities of 9-12 and loss tangents less than 1% were measured for all of the films investigated. The amorphous inorganic films prepared from solution compare well with vacuum deposited insulators currently in use.

Inorganic Resists

The ability to spin coat films with nanometer resolution that evolve into fully dense amorphous films led Stowers and Keszler to explore chemistry to enable these materials to be used as resists by adding peroxide to the solutions. [5] In the aqueous chemistry of metal oxides, peroxide is known to inhibit condensation reactions that would otherwise lead to precipitation. In these resist materials, beam induced decomposition and elimination of peroxide promotes condensation reactions, cross-linking of metal-oxo bridges, and the production of three dimensional framework structures. These frameworks produce the differential solubility between exposed and unexposed regions.



15-nm lines, LWR = 2 nm

Figure 3: A pattern of 15 nm lines with line with roughness of 2 nm.

With a 30-keV electron-beam, resist sensitivities as low as 8 $\mu C/cm^2$ have been realized using Hf and Zr based aqueous chemistries. At higher exposure doses, 15-nm lines and 36-nm dense features have been written with line-width roughness near 2 nm (Fig. 3). In comparison to more conventional polymer electron-beam resists, the high sensitivity achieved with these inorganic materials is remarkable. The sensitivity can be traced to their high electron densities, approximately 2.5 times that of the common organic photoresist poly(methyl methacrylate). Since the stopping power for an electron is proportional to the electron density of the resist, the ability to use heavy metals in the films is a distinct advantage.

As an added bonus, several of the inorganic resists tested have an etch resistance greater than 7 times that of thermal SiO_2 when using reactive-plasma etching. This resistance permits straightforward production of structures exhibiting exceptionally high aspect ratios.

Displays

The high performance of the Center's aqueous-processed dielectrics and semiconductors [1,2,6] has prompted industrial interest in their potential use as critical components of the driver transistors for large-area liquid crystal displays. Through work at Inpria Corporation and the Taiwan TFT LCD Association, the aqueous methods have been successfully transferred from the University setting, leading to successful integration and the production of several LCD panels on large-area G2 substrates (Figure 4). With mobilities exceeding 2 cm^2/Vs, the oxide transistors easily outperform the amorphous Si transistors found in current commercial displays. Again, each of the solution-processed layers in the oxide transistors was deposited at atmospheric pressure in air, eliminating the need for vacuum processing.

Figure 4: 4.1" AM-LCD with integrated IGZO semiconductor and AlPO dielectric

Center Education Program

The education program in the center introduces graduate students to semiconductor device physics, traditional silicon device processing, and the new inorganic based thin film technology being developed by the center in a 15 week intensive summer program. This immersion program has a large laboratory component designed to challenge students to solve complex problems. In the first part of the course, students work together to figure out how to make working MOSFET devices. In the second part of the course, amorphous inorganic films prepared from aqueous solutions replace the traditional elements in these devices.

Following this summer program, students are encouraged to take 6-9 month internships with companies that are partnering with the Center. These internships let the students see how the inorganic film technology is being applied. On returning to campus, the students have the option of working in partnership with the company with which they did the internship.

Conclusions

The Center for Green Materials Chemistry is developing novel solution precursors that enable fully dense and

pinhole-free thin films to be deposited from aqueous solutions. These films can be annealed at low temperatures, achieving high performance as condensation reactions densify the films. By adding reactive molecules to the initial solutions, the films can be directly exposed and developed, taking advantage of the solubility differences induced by the exposure technique. These inorganic resists are extraordinarily sensitive relative to their organic counterparts, due to the higher electron densities produced from the higher atomic number elements making up the films. Etch selectivity can be significantly increased relative to conventional materials by taking advantage of the diversity of chemistries found in the periodic table.

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