

Materials for Step and Flash Imprint Lithography

C. Grant Willson,^{*,1} Jianjun Hao,¹ Michael Stewart,¹ Yukio Nishimura,¹
Frank Palmieri,¹ Wei-Lun Jen,¹ Michael Dickey,¹ Andrew Chan,¹ Kai
Wu¹, John Ekerdt,¹ Jordan Owens,² Jeffery T. Wetzel,²

¹Department of Chemical Engineering, The University of Texas,
Austin, Texas 78712 USA

²The Advanced Technology Development Facility, 2706 Montopolis
Drive, Austin, Texas 78741 USA

Introduction

The continuing, nearly frantic race to produce ever smaller semiconductor devices has been quantified in Moore's Law and detailed in the International Technology Road Map for Semiconductors (ITRS). The force that motivates and drives this race is purely economic and derives from the fact that reducing the size of the circuit elements in these devices results in a corresponding reduction in the cost to manufacture them and at the same time, it improves the performance of the devices. The societal benefits of the technology developments that have derived from decades of investment of both intellect and dollars in this race are huge; they have changed the nature of life all over the world.

Every few years for the last three decades, soothsayers, nay sayers and skeptics have predicted an end to this exponential relationship between minimum feature size and time that is Moore's Law or at a minimum, a diminution in the rate of change. Of course, all of them have been proven wrong. The slope of the Moore's Law plot has actually steepened in the last decade! Will this continue? Can this continue? How long can it continue? Is there a limit to this scaling process? These are important questions. Certainly there is a fundamental limit to our ability to pattern materials. When the minimum feature size reaches one atom on width, we will surely have seen the end of this fascinating race. Already, it is possible to arrange single atoms into arbitrary patterns to produce features with a width of one atomic diameter. This had been accomplished in several laboratories using scanning tunneling microscopes to manipulate atoms on very cold surfaces. The ability to produce these tiny patterns has provided interesting and important fundamental data for studies in physics but the structures that can be built at this time can not be exploited to manufacture functional devices. In addition, the production of such patterns is painfully slow, many orders of magnitude to slow to support any sort of production of the sort we are used to imagining.

The process that limits the size of the minimum features that can be produced in manufacturing is photolithography. The resolution limit of this process is in turn controlled by the ability to produce lenses with ever increasing numerical aperture that focus light of shorter and shorter wavelength. The numerical aperture of the lenses used to project mask patterns on resist has evolved from 0.16 to 0.85 and greater and the wavelength of the light that is focused by these lenses has been reduced from 365nm to 193nm. There was recently a world wide effort to produce exposure tools and imaging materials that would enable exposure in the vacuum ultraviolet at 157nm but that effort has been abandoned. The industry proposes to take a huge jump in wavelength, by driving all the way from 193nm to a wavelength of about 10nm in the soft x-ray or "extreme Ultraviolet"(EUV) spectral region to exploit the discovery of multilayer coatings that reflect efficiently in this region of the spectrum. The development of the tools, materials and infrastructure necessary to manufacture devices with this wavelength of radiation is a daunting task but progress is being made. The first full scale EUV tools will be delivered for experimental use this year.

The EUV tools are very complex and there are a number of technical challenges remaining to be solved before they are viable. A single exposure tool of this sort is expected to cost more than twenty five million dollars and some estimates are more than twice that sum. The cost of building a factory based on these tools has been projected to exceed the gross national product of many countries. The technology may be available to continue down the path predicted by Moore's law, but will the economics of the market justify or support such expense?

An interesting, potentially disruptive patterning technology has emerged from laboratories recently. This technique called imprint lithography encompasses a variety of techniques that can be described

as embossing, stamping or molding. The resolution demonstrations provided by this technology are astounding and the tools are very much less expensive than the photolithography options. The technique is being studied in laboratories all over the world and several small companies have grown up that supply early versions of imprint lithography tools. This technology was recently recognized by inclusion in the ITRS. Time will tell whether imprint lithography is another "flash in the pan" or a truly disruptive technology that could extend the period that the industry can stay on the pace predicted by Moore's law. In large part, that will depend on the development of new materials.

Results and discussion

The version of this process called Step and Flash Imprint Lithography¹ (SFIL) involves use of a transparent, quartz template into which high resolution relief structures have been etched². The template is brought into proximity of a wafer surface and a photopolymerizable, low viscosity liquid is allowed to fill the gap between the template and the substrate. Blanket exposure through the back side of the template seves to cure the material and the template is removed to leave a high fidelity replica of the relief pattern on the substrate. The photopolymerizable material typically contains a significant amount of silicon and it is patterned over a layer of carbonaceous material. The imprinted pattern can then be transferred through the underlayer using standard, anisotropic etching steps to provide high resolution, high aspect ratio images.

The success of this process requires a unique set of materials properties. We have explored an acrylate platform and a vinyl ether platform both of which will be described. The acrylic formulation has been prepared from readily available, low volatility monomers chosen to provide adequate mechanical stability, etch resistance and reactivity. This approach suffers from certain limitations that are related to the fact that oxygen quenches this free radical mediated polymerization. This phenomenon is responsible for an induction period prior to onset to polymerization and the existence of a peripheral area, a border surrounding the exposed area that is not fully cured. A full kinetic model for this reaction has been developed³ that allows a study of the trade offs between the power of the light source power and these phenomena.

Photopolymerization of vinyl ethers initiated by photoacid generators offers an alternative design that circumvents the problems with acrylates.⁴ Unfortunately, the variety of commercially available silicon containing vinyl ethers that are useful for this application is limited so new materials had to be synthesized. These materials perform well and do not have a significant induction period but the force required to separate the template from the photopolymerized material is higher than that for acrylates. Incorporation of a fluorinated surfactant in the formulation and tailoring of the surfactant and the surface energy of the template to maximize migration of the surfactant to the template surface prior to polymerization offers an attractive solution to this problem.

Recent materials efforts have focused on the development of photopolymerizable materials that have high thermal stability and a low dielectric constant that can be used to imprint the dielectric layers in the interconnect layers of microelectronic devices. The unique ability of SFIL to define both a wire and a connector (via) in a single step offers the opportunity to remove over 100 steps from the process used to manufacture modern microprocessors. To that end, a variety of new, liquid polysilsequioxane cage compounds and photopolymerizable silicate precursors derived by sol gel oligomerization chemistry have been prepared and tested for this application. The progress of this synthetic work and the implementation of this process into a wafer process will be presented.

references

- [1] Colburn, M., et al, Proc. *SPIE: Emerging Lithographic Technologies III*, **3676(I)**: 1999.p 379.
- [2] Resnick, D. J.; Dauksher, W. J.; Mancini, D.; Nordquist, K. J.; Ainley, E.; Gehoski, K.; Baker, J. H.; Bailey T. C.; Choi, B. J.; Johnson, S.; Sreenivasan, S. V.; Ekerdt, J. G.; and Willson, C. G. *Proc. SPIE: Emerging Lithographic Technologies VI*, **4688**: (2002), p205
- [3] Dickey, M; Willson, C. G. *Chemistry of Materials* (accepted)
- [4] E. K. Kim, E.K.; Willson, C.G. *J. Vac. Sci. Technol. B* (accepted)