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SEMATECH Position Statement Regarding

The Business Case for the Continued Need of PFOS

There are two issues to the business case. The first is that advanced semiconductor manufacturing currently uses photoresist and antireflective coatings (ARCs). The second is that critical features have been shrinking according to a curve described as Moore's Law. This law, which is an observation of actual trends, states feature size shrinks by a factor of 0.7 every 2 to 3 years. This trend has been in effect for the last 30 years. In the 1990s, the size of minimum features actually became smaller than the wavelength of the light used to image them. This shrinkage required a more sensitive resist to produce the desired images. (The resist is like photographic film. When there is less light, either the exposure takes longer or the film must be faster. To maintain production speeds, the resist must become more sensitive.)

Creating images that are smaller than the wavelength of light poses significant challenges. High volume manufacturing necessitates an increase in the "film speed" of the resist. This is accomplished by incorporating PFOS (perfluorooctanyl sulfonates) into the photo-acid-generator (PAG) that increases the sensitivity of the resist. The semiconductor industry uses PFOS in its existing 248nm and 193nm photolithography processes.

(The generic class of chemical substances in which a sulfonyl group is attached to a completely fluorinated alkyl chain consisting of **n** carbon atoms is called perfluoroalkyl sulfonates [PFAS]. The eight-carbon homologue of the PFAS family is referred to as PFOS, which is a critical ingredient in existing semiconductor photoresists, ARCs, and photoresist developers and etchants)

The development of 248nm resist, which was the first resist to incorporate PFOS, was a major effort. First, a more sensitive material had to be found, and then the material had to be "hardened" to prepare it for use in high volume manufacturing. The 248nm effort was difficult for the semiconductor industry. The resist design started in the early 1980s. Although the resist formulations were ready for introduction into manufacturing by 1991, it took until 1995 to resolve all the issues to allow its use in high volume manufacturing. This illustrates how difficult it is to develop completely new resist formulations. With known chemical backbones for the resist, it takes about 8 to 10 years to develop a single resist and make it production worthy. This proposed ban would require the development of an entirely new backbone, which would increase the total time-to-market.

Current resist formulations contain approximately 1% PFOS. While research to reduce the PFOS content or to replace PFOS in resists continues, the prospect of going significantly below 0.5% PFOS content is not great and achieving less than 0.1% is outside the realm of current understanding.

There is another issue with creating very small images, especially those below the wavelength of the exposure radiation. The illumination to create these miniscule images results in unwanted features from surface reflections. To prevent these reflections, an

ARC is used. Without the ARC, the images are fuzzy and blurred like those seen in poorly made mirror. Another example of this effect is the haze that appears around lights at night when there is moisture in the air. This effect would destroy the features required for leading-edge devices. ARC comes in two versions: top ARC (TARC) or bottom ARC (BARC). Developing these materials is as difficult as developing the resist formulations.

PFOS in ARCs has two functions, both of which address light reflectivity. The first function is to keep light from reflecting in the resist, as discussed above. The second function is to keep unwanted light from creating spurious images. This is done by matching the index of refraction of the ARC to that of the resist. An additional benefit of PFOS is that it acts as a surfactant or leveling agent. This might appear to be minor compared to its light controlling features; however, that is not the case because the physics of coating are extremely complex. The leveling agent controls striation within the resist layers. Without this control, the images would be distorted. (The control required is equivalent to accurately replicating the width of a blade of grass in an area the size of a football field).

Typically, ARCs contain more PFOS than resists. The PFOS content in TARCs ranges from 2% to as high as 10%, with 5% being typical. BARCs have a slightly lower PFOS content. Based on existing chemistry knowledge, halogenated chain groups are ideal and the perfluorinated groups are best. Consequently, PFOS is critical component of leading-edge semiconductor manufacturing.

The introduction of new technologies generally relies on previously developed materials. The 193nm resists required more sensitivity than the 248nm. Future generations, whether 157nm, extreme ultraviolet (EUV), or some other wavelength, will require even more sensitive materials. The plan is to leverage previous development efforts and continue on the proven development cycle of 8 to 10 years. The semiconductor manufacturers that only employ longer wavelengths of light (e.g., I-line or 365nm) do not have the need for the sensitive resists. However, these are not the leading edge technology manufacturers.

The industry has been working diligently to reduce the PFOS content of materials by the development of alternatives. For example, some suppliers are now offering some PFOS-free materials. However, efforts to replace PFOS in resists and ARCs have not been very successful. Manufacturers are also evaluating newer formulations that employ other PFAS homologues such as the four-carbon chain molecule, but attempts to insert them into manufacturing have shown that they have much poorer performance than the PFOS containing materials. Considerably more engineering will be required to make the PFOS-free alternatives work in manufacturing; they will certainly not be “drop-in” replacements.

The total usage of PFOS per wafer continues to decline due to the fact that less resist is used per wafer. With the move from 200mm wafers to 300mm wafers, the area increased by 125%. However, new techniques for applying resist have decreased the amount of resist used from approximately 3ml per wafer to a volume that is approaching 1ml per wafer. Assuming the resist has a constant chemical composition, the effective reduction in resist use is 85% based on the area increase and the volume decrease.

The situation that needs to be examined is what happens if the industry were forced to eliminate PFAS homologues completely. Because there is no history of a completely PFOS-free material (much less a PFAS-free material) that can be used in manufacturing at the advanced technologies, there must be invention. However, relying on invention for developing a completely new material represents high risk and introduces great uncertainty in the development timetable.

Replacing the resist systems currently in use in advanced semiconductor manufacturing for 248nm and 193nm lithography would be very problematic. Again it would require extensive research and development followed by a time-consuming manufacturing process re-qualification. This combined effort could take over 15 years, but more probably 20 years. The likely outcome, if everything worked well, would be new materials ready for use by 2019.

The development cost of a new system—one resist system—for the industry has been estimated at $192M for 193nm resist, $287M for 157nm resist, and $218M for EUV resist. The cost for 157nm resist development is the highest, because it has more novel requirements than either 193nm or EUV resists. EUV development will build on existing 248nm and 193nm resists, but it is unknown whether these resist platforms will be adequate. If not, new novel materials will have to be developed requiring more time and money.

The second issue is introducing the new resists into high volume production. The technology introduction typically takes 18 to 24 months after the resist has been proven production worthy (capable of high speed production with acceptable yields.) The introduction process starts by producing a small volume of wafers and ramping the factory's production to full volume over 18 to 24 months. This is normally a time of improving yields. The exact data for technology introduction is proprietary information that varies from company to company. However, initial yields are typically well below 30% and take the full introduction time to reach 70% and higher. In full production, these yields will reach over 90%.

So far the industry has not had to change resists in the middle of a technology cycle, but if it had to, some assumptions can be made. Introducing a new resist requires an extensive qualification process. This qualification is costly and involves many engineers. If development engineers are working primarily on legacy resists, they cannot work on the newest technologies and the total technology development timeline will be impacted. This direct cost cannot be estimated, since it will vary by company. However, market costs associated with a resist infrastructure change can be projected, as illustrated below.

Scenario One: the change in resist infrastructure occurs simultaneously worldwide. Assume that the introduction yield starts at 30% and increases 3% per month over the next 18 months to a high volume production yield of 81%. A typical wafer manufacturer runs 20,000 good wafers per month (98% yield) in one fabrication facility (fab) with a value of $5,000 per wafer (totaling $100M per month). Over these 18 months, that fab would have generated $1.8B in revenue. Revenue for the fab converting to a new resist would have been approximately $1.1B, a reduction in contribution to the economy of $0.7B over the 18 months. Additional revenue would be lost as the facility increases its yield to 98% with current manufacturing methods. It would be more advantageous for the company to relocate the leading edge material to another site without restrictions. This would relegate the existing fab to older technology.

Scenario Two: only individual countries must change their resist infrastructure and other areas of the world do not. It has been shown that a delay in the introduction of a new product (i.e., the time-to-market) costs a manufacturer over $2M per day in profits for each day introduction is delayed. While this situation is not completely analogous to semiconductor manufacturing, it has many similarities. Since some manufacturers would provide products sooner (since they would no longer be on a learning curve), they would have a significant advantage (i.e., very early products receive a premium and then the cost per chip decreases as production volumes increase). If it takes 12 months to ramp to full volume, which is optimistic, the profit loss of a company still on a learning curve would exceed $500M. This is in addition to the normal revenue loss depicted in scenario one. Again, putting the company at a disadvantage for maintaining its fab in a location with a restriction.

Conclusion

The mandating of a specific cut-off date within a few years for the usage of PFOS would be detrimental to the European advanced semiconductor manufacturing. Expediting the existing research and development through specifically targeted funding could accelerate the learning curve and may reduce the projected 15 to 20 years for the development of replacement materials. Granting the semiconductor industry an exemption from the restrictions on the use of PFOS is prudent based on the industry's ability to tightly control the use of such substances and the limited total volume consumed. Without an exemption, the European community will be at a significant manufacturing disadvantage and leading edge technology will shift to regions that have exemptions or no restrictions on the use of PFOS. The net result is that the EU will lose high technology capabilities