Low-K Dielectric Materials for the Integrated Circuit Industry

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Hello and welcome to our WebCast on Low-K Dielectric Materials for the Integrated Circuit Industry. My name is Mary Haas. I'm a senior scientist in Air Products Electronics Technology Department. I'm a member of the Thin Films Team with a focus on development and optimization for our PDEMS Low-K offering. My address is listed on this title slide so you can please feel free to contact me if you would like more information.

In this section of our WebCast, we're going to focus on the basics of PDEMS. What is this material? What are its differentiating characteristics and how does Air Products use fundamental chemistry and material science knowledge to develop optimum materials?

As we move to the next technology nodes in integrated circuit manufacturing, we know there's an industry-driven need for lower dielectric constant materials. Silicon oxide was the industry standard for years and this material has a dielectric constant just above 4.0. It has excellent mechanical strength. It has good compatibility, but of course it has a limited dielectric constant. To get below a dielectric constant of 4.0 either fluorine or organic terminal groups can be substituted onto the silicon oxide matrix. These bonds are less polarizable and also they lower the overall density of the material.

So organic silicate glass films or OSGs can reach dielectric constants down to about 2.6. You can see from the plot we're showing here that the films become less mechanically robust as the dielectric constant decreases. Overall in designing these materials, it's a constant balance for us between lowering the dielectric constant while still maintaining integrable mechanical properties.

For the 45 nanometer node and beyond an even lower dielectric constant—somewhere around 2.5 or less is needed in order to reach desired device performance. One of the solutions to this materials problem is to add porosity to a Low-K material. The dielectric constant of air is 1.0, so if we make a composite of air in something like an organic silicate glass, we can achieve a material with an effective dielectric constant that's less than 2.5. It's a great idea although it's certainly not a trivial thing to do.

First, adding porosity to the film dramatically lowers mechanical properties like modulus and hardness. Therefore, it becomes even more critical to design a material that has an optimal balance of the dielectric constant and high mechanical properties.

Second, this porous technology was developed originally for spin-on type polymer materials. However, Air Products has invested over 5 years of R&D efforts in order to come up with a manufacturable PECVD solution for porous Low-K, and this really gives our customers the advantage of using their existing plasma deposition technology for future generation nodes.

Air Products has a wealth of chemistry and materials science skills that support our Low-K project. Part of this involves design of target materials using a foundation of modeling predictions. For example, if you look at the figure on this slide, you'll see that as porosity is added to a given material, the mechanical properties drop off at much faster rate than the dielectric constant. To compensate for this effect, we realized that it would be vital to really maximize our starting mechanical properties. Therefore, we designed a material with the highest degree of network connectivity and lowest organic content that we could achieve for a given dielectric constant. Each time you add a terminal group to the network, such as a methyl species, your overall bond density decreases and therefore your modulus decreases as well. So it's preferable to limit the number of terminal groups in the porous network. However, again, this is a constant balancing act because a threshold of carbon content is required in order to keep the hydrophobicity of the film and prevent water adsorption.

We're able to screen network connectivity by integrating the appropriate peak areas from FTIR and by comparing the density of terminal bonds (which in this case is silicon-methyl) to the density of network bonds (which in this case would be silicon-oxygen-silicon). We come up with a ratio that we call network connectivity. So one of the first steps in designing an optimal Low-K material is applying this network connectivity principle to the organic silicate precursor. As a chemical company we're able to screen a broad range of OSG precursors and look at the resulting network connectivity and mechanical properties. This includes designer precursors that we actually synthesize here on site. And what we find is that for a given dielectric constant, Diethoxymethylsilane (which we've trademarked as DEMS^{TM}), results in the lowest methyl incorporation and therefore the highest mechanical strength. We've developed our porous process around the DEMS^{TM} precursor in order to maintain a high degree of network connectivity and the best balance of properties.

A porous film requires the co-deposition of two materials. One is the organo-silicon precursor. This forms the matrix of the Low-K film. And the second is an organic plasma polymerizable material that ends up acting as a sacrificial porogen. The materials are introduced into the reactor chamber at the same time and they form a composite. Then after the deposition, the sacrificial porogen in removed, and it leaves pockets of air and finally it leaves a porous material. Once again, it's not a trivial process. The two precursor materials have to have overlapping process windows and the porogen also has to be deposited in such a way that we can remove it readily after the deposition.

The Air Products PDEMS^{TM} process, in particular, uses PECVD (Plasma Enhanced Chemical Vapor Deposition), to deposit Diethoxymethylsilane together with an organic porogen. And then in our process we remove the porogen using ultraviolet exposure. Ultraviolet removal of the porogen species has a number of benefits. As you can see on this slide compared to thermal treatment alone, it improves the final mechanical properties of the film up to even 50%. During the UV exposure the matrix experiences some densification and some portion of the terminal methyl groups are stripped from the matrix. Both of these effects which you can see on the slide result in a higher film modulus without significant impact to the dielectric constant. In addition, UV exposure is more efficient than a thermal treatment. Porogen can be removed from the film in a fraction of the time as a thermal treatment, with up to 10X faster throughput, which of course is very important to our customers.

As described previously, the network connectivity provides information about the resulting mechanical properties. So in addition to FTIR, we also use solid state NMR to examine our network. Here we show the NMR signals for a 2.5 dielectric constant film before and after we've removed the porogen from it. These data indicate that most of the organic species in the film are incorporated as mono-methyl silicon (as opposed to dimethyl or trimethyl), and this is arguably the favorable configuration for materials properties. We can also see a reduction in total methyl content after ultraviolet exposure. Additional NMR data that are not plotted here tell us that the matrix of a dense DEMS^{TM} -only film is highly similar to that of porous DEMS^{TM} film. This supports our hypothesis that the beneficial materials properties of our DEMS^{TM} precursor also translate to the porous film; even though the porous film undergoes a different set of process conditions and a highly energetic UV cure.

It's important to note that the dielectric constant of the porous film can also be tuned by varying the volume ratio of the two chemical precursors. As the percent porogen in the composite material increases the resulting dielectric constant is lowered. On this plot we show dielectric constants of 2.65 down to 2.0 for a mixture of DEMS^{TM} and our porogen, alpha-terpinene, and only slight process condition changes are needed to achieve the different dielectric constants on the plot. Most importantly, the process is highly extendable to future technology nodes without any additional changes to the chemical identities.

On the last slide we just saw that the ratio of porogen precursor in the feed has a strong impact on the resulting film. We also saw earlier that the OSG precursor DEMS^{TM} has a strong impact on mechanical properties. It turns out that the identity and chemical nature of the porogen precursor as well has a significant impact.

Here we're plotting modulus and network connectivity of DEMS^{TM} films that were deposited using 5 different porogen precursors. You can see, depending on the precursor that was used, the modulus is improved by almost 40% for a given dielectric constant. We hypothesize that the chemical nature of the porogen in the plasma, such as the fragmentation pattern and the energy capture, affects the deposition of the OSG precursor simultaneously. In this way the choice of porogen precursor can affect the final methyl content of the network, and therefore it can affect the mechanical properties of our film.

A final important materials property that may strongly impact integration is the nature of the porosity in the film. The pore size and the pore distribution can be modeled by observing the interaction of a beam of positroniums with the porous film, which is known as PALS. The mean-free path and subsequent annihilation of the positron is related to the pore size in the film. Also you can see in the slide the total volume porosity of a porous film can be measured using ellipsometric porosimetry.

Here we observe the change in refractive index as pores are filled with a solvent such as toluene. These aspects of porosity and morphology can impact the films materials properties, and can impact interaction with other processing steps during fabrication. So it's pretty important for us to arrive at an understanding.

One of the insights that we've gained by using ellipsometric porosimetry is that the chemical network of dense and porous DEMS™ films are very similar. By measuring the volume porosity of the film we can calculate the actual matrix dielectric constant of the network. You can see in the figure that the dielectric constant of the matrix as well as the combination of porosity is what gives you the measured dielectric constant k effective. What we find is that the matrix dielectric constant for porous DEMS™ falls on the same plot as the measured dielectric constant for non-porous DEMS™. In combination with NMR data this indicates that chemical and structural nature of dense DEMS™ and porous DEMS™ networks are nearly indistinguishable.

We saw earlier that changing the porogen precursor can impact the mechanical properties of a porous PECVD film, and here we use the PALS technique to look at the pore size and to look at the pore interconnectivity for DEMS™ films that we've deposited using 5 different porogen precursors. You can see that as we change the porogen precursor, we affect the pore size and we affect the pore interconnectivity. As we would expect, a higher volume porosity results in higher pore connectivity, but we also find that for a given total porosity, a smaller pore size results in higher pore connectivity. Although this may not be intuitive, our modeling results indicate that it can be due to the impact of a minimum wall thickness that can be supported in an OSG matrix. To achieve a given porosity, you need more small pores than you do large pores and on average the smaller pores will end up closer together. At some minimum wall thickness they'll start to collapse. Finally for a given dielectric constant we find that maximizing the network connectivity is vital to achieving the best mechanical properties, and it's probably even more important than minimizing the total porosity.

So in this WebCast we've tried to give a snapshot of our PDEMS™ Low-K offering, and we've tried to give a snapshot of the development behind it. Our team at Air Products uses structure property relationships and uses our foundation of chemistry and material science knowledge to design our materials. This knowledge also helps us work closely with our customers to tailor properties that are vital to their specific integration schemes.

Thanks for joining us on this WebCast. We hope that you found some valuable information and as you saw on the title slide you can please feel free to contact me at my e-mail address or you can look at the Air Products website to get lots more information. Thank you.