Vibrational Spectroscopy Of Ultra-Low-k Dielectric Materials

Special **ULK** Focus

FTIR and Raman spectroscopy are complementary vibrational spectroscopy techniques that help elucidate the molecular bonding and molecular structure in low-k materials. Raman spectra arise from inelastic scattering of the incident energy from a laser source, as a function of molecular vibrational energy. FTIR spectra arise from absorption of polychromatic radiation at specific energies of molecular group vibrations. Due to different selection rules, the two techniques are sensitive to different types of bonding and molecular geometries. In organic polyphenylene ultra-low-k (ULK) materials, Raman spectroscopy probes the amount of cross-linking by following the disappearance of a polyfunctional acetylene precursor, whose acetylene carbon-carbon stretching occurs at ~2200cm^{-1}, as a function of cure. Silsesquioxane low-k materials have the general formula ($RSiO_{1.5}$)n. FTIR spectroscopy monitors and quantifies the methyl, Si-CH_3, and Si-O-Si groups. These occur at ~2980 cm^{-1} (-CH_3 stretching), ~1275-1250 cm^{-1} (Si-CH_3 deformation), and ~1140-1030 cm^{-1} (Si-O-Si asymmetric stretching). The Si-O-Si stretching region of the FTIR spectrum contains information about bond angles and distributions. Curve-fitting analysis of this region provides a measure of the relative amounts of different geometries in the Si-O-Si microstructure. FTIR also measures chemical changes due to oxidative plasma processes that create damage in the dielectric films, such as carbon depletion from demethylation and silanol formation from oxidation of the Si-C bonds.

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Introduction

Ultra-low-k materials are polymeric compounds that can be either spun-on from solution or plasma deposited in a CVD (chemical vapor deposition) process. The dielectric constant is dependent upon both the film chemistry and porosity. Properties such as hardness and modulus also are related to the film chemistry, in terms of the composition, stoichiometry, and the cross-linking or degree of cure of the polymer.

Determination of the film chemistry is usually accomplished from a complementary analytical approach employing techniques such as RBS (Rutherford backscattering) and HFS (hydrogen forward scattering) for atomic composition, Auger or ToFSIMS (time of flight secondary ion mass spectrometry) depth profiling for elemental composition uniformity from top to bottom of the film, and FTIR (Fourier transform infrared) and Raman spectroscopy for determination of the molecular bonding chemistry within the film. The latter two techniques are complementary vibrational spectroscopy techniques.

FTIR is an absorption spectroscopy that measures the amount of absorption of infrared radiation as a function of molecular vibrational energy. The absorption peaks arise from specific molecular vibrations, and the intensities are proportional to the absorption cross-section which depends upon the amount of change in the electric dipole of the (molecular) group during the vibration. The absorption spectra allow for straightforward quantitation of the molecular groups, since the peak areas are directly proportional to the product of the absorption cross-section, film thickness, and concentration (Beer's Law).

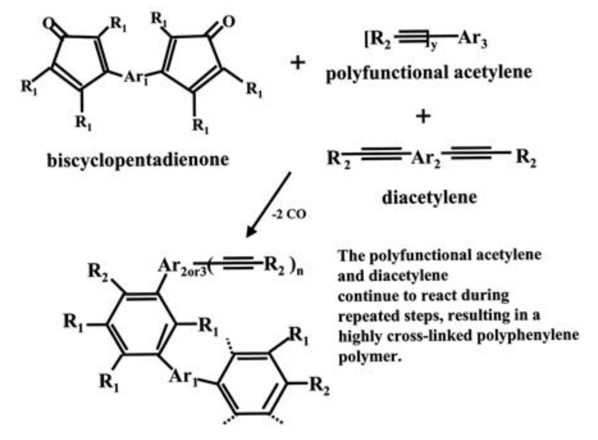
In Raman spectroscopy, the spectrum arises from a scattering process in which the radiation source is usually a visible or UV laser and the spectrum is a measure of the inelastic scattering (in which a small amount of the laser source energy is transferred to the sample) as a function of molecular vibrational energy. The scattering cross-section is dependent on the change in the electronic polarizability during the molecular vibration. Though quantitation is not so straightforward as FTIR, semiquantitative results can be obtained if peak intensities are normalized to a suitable internal reference.

Thus, both FTIR and Raman spectroscopy provide a picture of the molecular structure and chemical functional groups within a material. Their utility is dependent upon the molecular structure and symmetry in the material. Generally speaking, chemical groups that are unsymmetric in their molecular structure and undergo a large change in electric dipole during molecular vibration tend to be strong FTIR absorbers and weak Raman scatterers. Materials that are symmetric in their molecular structure and undergo a large change in electron polarizability during vibration tend to be strong Raman scatterers and weak FTIR absorbers.

Additionally, both FTIR and Raman measurements can be performed in microprobe mode by coupling a microscope to the spectrometer. FTIR microanalysis can be done on features as small as 10 microns; the Raman microprobe can analyze areas as small as 1 micron.

Vibrational Spectroscopy of Organic Polyphenylene-Based ULK Materials

Organic polyphenylene polymers can have k values around 2.1-2.6, depending on the specific chemistry and porosity of the material. The starting materials in the precursor contain a cyclopentadienone cross-linking agent, an aro-



The polyfunctional acetylene and diacetylene continue to react during repeated steps, resulting in a highly cross-linked polyphenylene polymer.

Figure 1. The phenylene cross-linked polymer is prepared from the reaction of the biscyclopentadienone, a polyfunctional acetylene, and a diacetylene. R_1 and R_2 are typically H, or an unsubstituted aromatic group. Ar_1, Ar_2, and Ar_3 are independently an unsubstituted aromatic moiety or inertly substituted aromatic moiety.

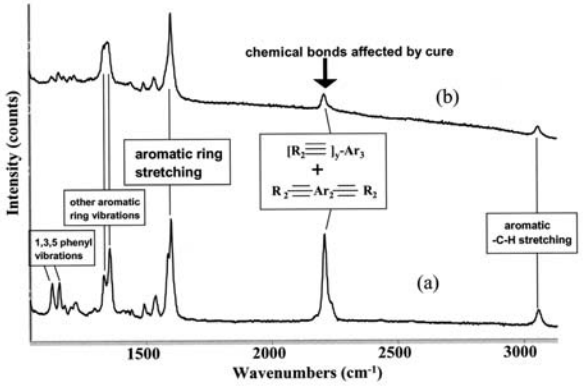


Figure 2. Raman spectrum of polyphenylene ultra-low-k dielectric: (a) Spun-on film, post-soft-bake but no cure; (b) same film, after furnace cure. The polyfunctional acetylene group is noted on the spectra and decreases in intensity as the cure progresses. The degree of cure is monitored by taking the ratio of the acetylene peak intensity at ~2200 cm^{-1} to the aromatic ring peak intensity at ~1600 cm^{-1}. Spectra were collected using 633 nm excitation.

matic acetylene containing three or more acetylene moieties and, optionally, a polyfunctional compound containing two aromatic acetylene moieties. [1] The precursor solution is spun onto the wafer, then soft baked and finally cured to achieve a cross-linked polyphenylene product. A generalized reaction scheme is shown in Figure 1. Through intermediate Diels-Alder cycloaddition reactions, acetylene branches of the polyfunctional acetylene monomers are repeatedly consumed. The progress of the cross-linking reaction is readily followed using Raman spectroscopy, which is a very sensitive probe for the presence of the acetylene functional group (Figure 2). The cure state is monitored by following the decrease in the acetylene groups at ~2200 cm^{-1}, normalized to the aromatic ring stretching bands at around 1600 cm^{-1}. The FTIR spectrum, on the other hand, does not reveal the acetylene chemistry, because selection rules forbid the vibrational transition in this group due to symmetry considerations. The Raman ratio of peak intensities at 2200 cm^{-1} to 1600 cm^{-1} has also been shown to correlate well with inline refractive index measurements using spectroscopic ellipsometry.

Vibrational Spectroscopy of Polymeric Silsesquioxane-Based ULK Materials

Silsesquioxanes are represented by the generic formula $(RSiO_{1.5})n$. Each silicon atom is bound to an average of one and a half (sesqui) oxygens and to one hydrocarbon group (ane). They can exist in the form of polycyclic oligomers and as polymers. Ultra-low-k materials made from these materials are typically HSQ (hydrogen silsesquioxane, R=H) or MSQ (methyl silsesquioxane, $R=CH_3$). Whether spin-on or CVD, the silsesquioxane-based ULK materials have the same general chemistry as shown in Figure 3.[2,3] Methyl silsesquioxanes contain Si-O-Si linkages and also $Si-CH_3$ groups. FTIR spectroscopy provides detailed information about the molecular bonding in the film, as indicated in the spectra shown in Figure 4. The CH_3 functional groups exhibit both stretching (around 2980 cm^{-1} and 2850 cm^{-1}) and bending features (around 1410 cm^{-1}). The $Si(CH_3)x$ functionality is discerned from the bending region, around 1275-1250 cm^{-1}, and the Si-C stretching region around 880-750 cm^{-1}.[4] k values in dense silsesquioxane-based ULK materials are affected by the carbon content, so increased methyl and Si-C functionality are correlated to lower dielectric constants.

The Si-O-Si bonding in MSQ and HSQ films is a complex chemistry containing both polycyclic and ladder type structures, and in some cases, also linear chains. Relative amounts of cage type (polyhedral) and network type (cross-linked ladder and linear chain structures) bonding affect mechanical properties such as hardness and modulus; higher network type bonding tends to produce a higher modulus film. In the FTIR spectra, the Si-O-Si cage and network structure show peaks in the 1200-1000 cm^{-1} region, consisting of overlapping bands from the distribution of local bond types and bond angles that exist in the micro-structure. Curve-fitting can help elucidate this structure, as shown in Figure 4. In tetrahedral $Si0_2$, such as thermal oxide, the Si-O-Si bond angle is 144 degrees, and the Si-O asymmetric stretch peak position is at 1080 cm^{-1}. In more cage-like structures, the Si-O-Si bond angles open to 150 degrees or greater, and the Si-O-Si peak position shifts to higher frequency, sometimes as high as ~1180 cm^{-1}. In more network-like structures, the bond angle reduces to <144 degrees and the Si-O peak position shifts downward in energy, to ~1030 cm^{-1}[5,6] The frequency in SiO (where x=1) is around 940 cm^{-1}.[7]

Other information obtained from FTIR characterization of these materials includes analysis of plasma-damaged films (Figure 4b). Plasma oxidation of the $Si-CH_3$ groups leads to formation of Si-OH groups. Both isolated and hydrogen-bonded silanol groups are typically observed, giving rise to -OH stretching bands at around ~3750 cm^{-1} (isolated -OH) and broad bands in the ~3500 cm^{-1} region (hydrogen-bonded -OH); an Si-OH bending band is observed at around 935 cm^{-1}. Carbon

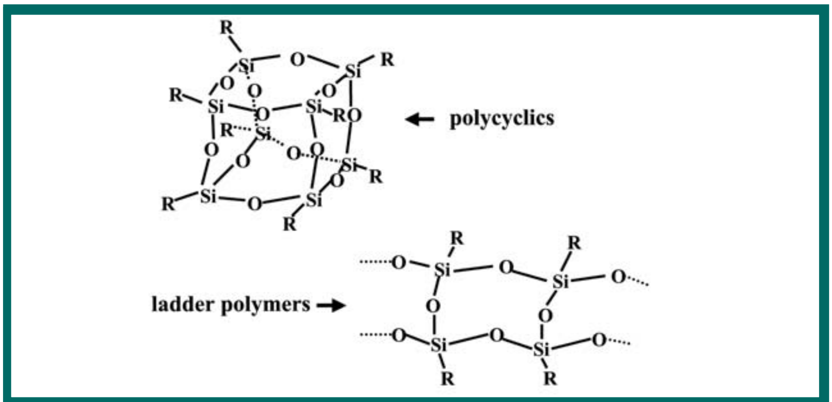


Figure 3. A generalized schematic for polysilsesquioxane structures. Polycyclics and ladder structures, as well as linear chains (not depicted) can all be present in a silsesquioxane-based ULK material. Each silicon atom is bound to an average of one and a half oxygens and to one hydrocarbon group (represented by R).

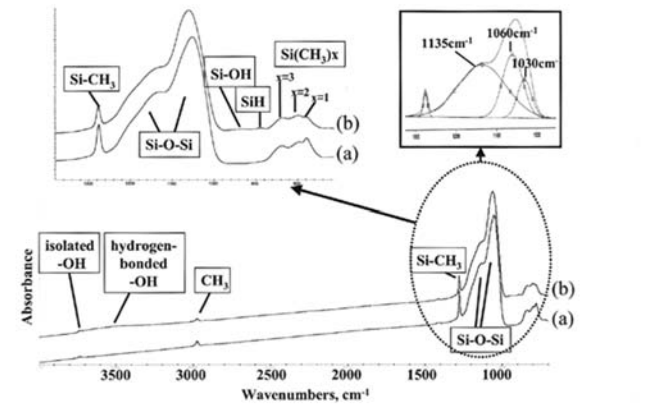


Figure 4. FTIR spectra of an MSQ ultra-low-k dielectric: (a) film as deposited; (b) film post oxygen plasma process. After plasma, the film becomes hydrophilic and features due to isolated and hydrogen-bonded hydroxyl appear in the spectrum, giving rise to bands ~3750 cm^{-1}, 3500 cm^{-1}, and a weak band around 935 cm^{-1}. A small amount of Si-H forms from the plasma treatment, as evidenced by the weak Si-H wagging band at ~890 cm^{-1}. Carbon depletion is indicated by loss of -CH$_3$ and SiCH$_3$ intensities. The various methyl substitutions on Si are indicated in the Si-C stretching region where Si(CH3)$_3$ occurs at 837 cm^{-1}, Si(CH3)$_2$ at 797 cm^{-1}, and SiCH$_3$ at 779 cm^{-1}. The inset in the upper right shows results of curve-fitting to deconvolve the Si-O-Si stretching region.

depletion from plasma damage is observed as demethylation, leading to intensity losses in the CH$_3$ and Si(CH$_3$)x vibrations in the FTIR spectrum. Attempts to repair the damaged region by restoring methyl functionality, through chemical treatments, can be monitored and quantified using FTIR spectroscopy to assess the amount of bulk repair to the film chemistry in the reaction of -OH bonds with reformation of methyl and Si(CH$_3$)x bonds.[8]

Vibrational Spectroscopy Of Porous ULK Materials

Further reduction of the dielectric constant in ULK materials is obtained from the introduction of porosity into the structure. In CVD materials this may be accomplished by flowing a porogen as an additional precursor component into the plasma mixture. The porogen is then removed by a post deposition burnout process that can be either a thermal treatment or some other energetic process. (Electron beam or photon exposure can sometimes be used.)

The determination of residual porogen is best done by sensitive outgassing analysis techniques, such as thermal desorption mass spectrometry. Vibrational spectroscopy is useful for determining changes in the bulk film chemistry, other than porogen removal, such as demethylating a methylsilsesquioxane polymer, or altering the cage to network Si-O-Si bonding structure. In addition, depth profiling techniques such as Auger spectroscopy and ToFSIMS should also be used to characterize the compositional changes in the film from top to bottom, after porogen burnout.

Conclusion

FTIR and Raman spectroscopies offer insights into ULK material properties by characterizing the molecular bonding and chemical microstructure. In polyphenylene polymers, Raman spectroscopy monitors the amount of cross-linking or degree of cure. With silsesquioxane polymers, FTIR monitors as-deposited film chemistry and post processing chemical changes such as hydroxyl formation or demethylation from plasma damage. Vibrational spectroscopic analysis together with complementary depth profiling techniques such as Auger and ToFSIMS give a very complete picture of ULK film chemistries, which help semiconductor development and integration engineers to make critical material and processing decisions.

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Biography

Nancy Klymko received her Ph.D. in chemistry from the University of Michigan, and joined IBM in 1981. After two years in the resist product engineering department, she joined the technology analysis organization in East Fishkill. She has enjoyed many years in this organization as part of the chemical analysis, process analysis, and structural physics groups. During this time, she has been involved in a broad scope of materials characterization and problem-solving for both semiconductor and packaging technology programs.