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Effects of Precursor Additives on the Stability of PECVD Deposited a-GeC:H Films

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Effects of Precursor Additives on the Stability of PECVD Deposited a-GeC:H Films

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ABSTRACT

Germanium and carbon based films have been deposited by plasma enhanced chemical vapor deposition (PECVD) from tetramethylgermane (TMGe) with additions of oxygen, hydrogen or argon. The index of refraction, extinction coefficient and optical gap and FTIR spectra of the films have been measured as well as their stability in regular ambience. It was found that the films deposited from pure TMGe were stable in time only if deposited at a negative bias above -250 V DC. Films deposited at a bias of -150 VDC could be stabilized by significant additions of oxygen to the plasma and complete stabilization was achieved at O₂/TMGe ratios larger than 3 in the gas feed. Additions of hydrogen or argon to TMGe had only slight effects in improving the stability of the films.

I. INTRODUCTION

Amorphous films based on group IV elements have been studied extensively and have found a variety of electronic, photovoltaic, optical, and mechanical applications. This is true for amorphous hydrogenated silicon (a-Si:H), amorphous hydrogenated carbon (a-C:H), and their alloys (a-SiC:H). However, amorphous hydrogenated germanium carbon (a-GeC:H) films have been less investigated. Characteristics of such films prepared by sputtering have been reported in several studies^{1,2} while properties of a-GeC:H films prepared by plasma enhanced chemical vapor deposition (PECVD) have been reported in.³⁻⁷ The studies of films prepared by rf PECVD from tetraethylgermane (TMGe) or tetramethylgermane have found that the film properties are strongly dependent on the deposition conditions, especially on the power input to the plasma used for their preparation.⁵⁻⁷ The films prepared at low energy input to the plasma were soft, semitransparent, had a relatively low density (around 2.0 g.cm⁻³) and an electrical conductivity below 10⁻¹⁰ S.m⁻¹. At high rf power the films became stiff, non transparent, their density rose to about 3.5 g.cm⁻³ and their electrical conductivity to about 10⁻⁴ S.m⁻¹.⁶ Furthermore, the films prepared under low power input underwent an aging process in the ambient atmosphere and their properties changed with time. The authors attributed this behavior to the existence of substantial amounts of dangling bonds in the as-deposited a-GeC:H films, which, upon exposure to the atmosphere, got saturated with atmospheric oxygen with the formation of Ge-O bonds. The aging

caused a reduction of the density of the localized states in the bulk of the film as well as a drastic decrease in the surface states.^{6,7}

Any practical application of a-GeC:H films will require film stability. It was therefore the scope of the present study to investigate the potential of stabilizing these films by several approaches based on the addition of several gases to the films precursor: (i) oxidation of the films during the deposition process by addition of oxygen to the plasma; (ii) passivation of the dangling bonds by addition of hydrogen to the plasma; (iii) modification of films structure by enhanced ion bombardment through addition of Ar to the plasma. The properties of the films deposited with these additives and their stability in air are reported next.

I. EXPERIMENTAL

The a-GeC(X):H films (X = none or O) were deposited from tetramethylgermane (TMGe) or mixtures of TMGe with O₂, H₂ or Ar in a parallel plate rf PECVD reactor. The films were deposited on Si substrates placed on the powered electrode, where they acquired a negative bias.⁸ The deposition was performed under bias control in order to control the bombardment of the growing film with the energetic ions from the plasma. As the films were deposited at constant pressure, the power applied to the plasma increased with increased substrate bias. After performing the deposition of films from pure TMGe over a range of substrate biases, it was established that the boundary between stable and unstable a-GeC:H films is between -150 V DC and -250 V DC (the DC designation will be dropped in the following but with the understanding that the bias values are DC volts). The study was therefore continued for films deposited at these two biases.

It was assumed previously that the instability of the a-GeC:H films deposited at low power or bias is caused by film oxidation in air over time.⁶ By adding sufficient oxygen to the plasma during the deposition process, we expected to complete the oxidation reaction during film growth and produce stable films.

The instability and subsequent oxidation of the films deposited from pure TMGe is supposed to be due to the existence of Ge dangling bonds within the amorphous network.⁶ As hydrogen is known to have the potential of passivating dangling bonds we decided to investigate the impact of H₂ addition to TMGe on the stability of the a-GeC:H films.

Another possibility of improving the stability of the amorphous films is to modify them through bombardment with positive ions during deposition. Addition of Ar to the plasma enhances the ion bombardment of the growing film which could in turn remove weakly attached species and produce more organized films, containing less dangling bonds. It was therefore assumed that films grown from mixtures of TMGe with Ar will be more stable than pure TMGe films. Argon was chosen for its high atomic weight, to make the effect of the ion bombardment enhancement

efficient. The specific conditions used for the deposition of the different samples are provided in Table I.

Fourier transform infrared absorption (FTIR) analysis was used to identify the different bonds in the investigated films. A *n&k Analyzer* apparatus was used to determine the index of refraction (n), extinction coefficient (k), optical gap (E_{opt}) and film thickness. The film thickness was verified separately by measuring the height of a step produced in the film. Rutherford backscattering (RBS) and Forward recoil elastic scattering (FRES), in combination with the thickness data, were used to determine the density films.

The different film characteristics were measured within one hour after deposition and then over different time intervals, to more than one month. The density of the films could be determined only after an exposure to the air of more than two weeks. The stability of the films was deduced from the evolution over time of the optical gap and of the FTIR spectra. The index of refraction and extinction coefficient at 633 nm did not change significantly with time for any of the studied films and could therefore not be used to assess the stability of the films.

III. RESULTS AND DISCUSSION

III.a. Properties of as-deposited films

The densities of the investigated films are presented in Figure 1 for the two deposition biases. It can be seen that, for all precursor mixtures, the density of the films increases with increasing deposition bias. The density of the films deposited from pure TMGe at -150V was 2.25 g.cm^{-3} , increasing to 2.5 g.cm^{-3} for the film deposited at the bias -250V. The higher rf power associated with the higher bias results in stronger dissociation of the TMGe precursor in the plasma. The films deposited at the higher bias are therefore formed from smaller precursor fragments and are thus more compact than films formed from larger fragments in the lower bias/lower power plasma. This will be latter demonstrated by the FTIR spectra which will show that the films deposited at -150 V contain larger fractions of Ge-CH₃ bonds than the films deposited at -250V. Incorporation of such structures in the films results in the formation of less denser films. Stronger ion bombardment of the films growing at the higher bias can remove weakly bonded species at the surface of the films and further densify the films.

The density of the films deposited form mixtures of TMGe+O₂ increases with the amount of oxygen added to the gas feed, reaching values of 3.2 g.cm^{-3} for the films deposited at -150 V, and 3.6 g.cm^{-3} for the films deposited at -250 V. The films deposited at -250 V were denser than those deposited at -150 V, for any oxygen flow.

The increase of the films density with increasing O₂/TMGe ratio in the gas feed is an indication that the films become more similar to germanium oxide, which is characterized by a density of 4.2 g.cm^{-3} in the hexagonal phase.⁹ We shall see later that the stability of the films

deposited at a bias of -150 V correlates with their density and the films whose density is greater than 3 g.cm^{-3} are stable.

The density of the films deposited from mixtures of TMGe+H₂ is also increasing with increasing H₂/TMGe ratio. However, the density reaches a low value of 2.75 g.cm^{-3} at a H₂/TMGe ratio of 3 as compared to 3.05 g.cm^{-3} for a film deposited from TMGe+O₂ at the same flow ratio (see Figure 1.a). Addition of Ar to TMGe also increases the density of the films deposited at -150V, but to a smaller extent than the additions of O₂ or H₂.

The optical properties of the as-deposited a-GeC:H films are given in Table I, where it can be seen that the deposition bias significantly affects all optical properties. The index of refraction and the extinction coefficient increase while the optical band gap decreases when the negative deposition bias increases in absolute value. The n and k values of 1.95 and 0.00 of the films deposited from pure TMGe at -150 V increase to 2.68 and 0.087, respectively, for the film deposited at -250 V. The optical bandgap of the same films decreases from 2.6 eV to 1.84. A similar behavior was reported previously elsewhere for a different deposition system.⁵

Figures 2 and 3 present the indexes of refraction and the extinction coefficients and Figure 4 presents the optical bandgap of all the studied films. It can be seen in Figure 2 that, for the films deposited from mixtures of TMGe+O₂, the values of the index of refraction are higher for the films deposited at -250 V than for the films deposited at -150 V in the O₂/TMGe range 0 - 6 and about equal for O₂/TMGe ≥ 6 . The optical gap varies the opposite way with O₂/TMGe as shown in Figure 4. The extinction coefficient of all the a-GeCO:H films is zero. Figures 2.a and 4.a indicate that the effect of oxygen addition to TMGe saturates at an O₂/TMGe ratio of 0.5 for the films deposited at -150 V, while the effect is continuing with the ratio increasing up to 10 for the films deposited at -250 V. However the final values reached in both cases are about the same. It thus appears that for the less denser films deposited at -150 V small addition of oxygen to the plasma have a strong effect in oxidizing the film, while the process is more gradual and requires larger amounts of oxygen in the denser films deposited at -250 V.

The effect of the H₂ addition to TMGe on the optical properties of the a-GeC:H films is opposite to that of O₂ addition. For the films deposited at -150V, the refractive index and extinction coefficients increase and the optical gap decrease with increasing H₂/TMGe ratio. For H₂/TMGe varying from 0 to 3, n increases from 1.95 to 2.21 and E_{opt} decreases from 2.60 eV to 2.09 eV (see Table I and Figure 2.a). The effect of H₂ addition is much less pronounced for the films deposited at the higher bias of -250V (see Figure 2.b).

Addition of Ar to TMGe, up to a ratio Ar/TMGe=2, has a much smaller effect on the optical properties of the films. The Ar addition to the plasma slightly increases n and k and slightly reduces E_{opt} for the films deposited at -150V and has no effect on the films deposited at -250V.

The studied a-GeC:H films have an amorphous structure comprised of a random covalent network of Ge, C and H atoms and containing single or multiple Ge-Ge, Ge-C, C-C, Ge-H and C-H bonds. FTIR absorption measurements were performed in order to identify the bonds in the

films and their variation with the deposition conditions and time. The assignment of the identified FTIR peaks is given in Table II and discussed next.

The FTIR spectra of as-deposited a-GeC:H films are presented in Figure 5. Both as-deposited films present absorption peaks corresponding to the different bonds: C-H at 2970, 2905, 1450, 1410, 1360 cm^{-1} , Ge-H at 2005 cm^{-1} , C=C at 1570 cm^{-1} , Ge-C-C at 1000 cm^{-1} , Ge-CH₃ at 1240 and 780 cm^{-1} . However, the film deposited at -150 V (Figure 5.a) has an additional peak at 830 cm^{-1} which will be identified later as belonging to a Ge-O bond.

The comparison of the spectra of the films deposited at -150 V and -250 V shows that the film deposited at the higher bias contains less CH₃ (2970 cm^{-1}) and more CH₂ (2910 cm^{-1}), slightly more Ge-H (2005 cm^{-1}), much less Ge-CH₃ (1230, 780 cm^{-1}), and much more C=C (1570 cm^{-1}) and C-C (1025 cm^{-1}) bonds. Furthermore, the Ge-H peak at 2005 cm^{-1} is shifting towards the lower wavenumbers at 1980 cm^{-1} with increasing bias. The observed changes reflect variations in the plasma with the different applied substrate biases. The higher rf power corresponding to the higher bias results in stronger dissociation of the TMGe molecule, hence more fragmentation of its Ge-C bonds and stronger dissociation of the C-H₃ bonds. The films deposited at the higher bias, therefore contain less Ge-CH₃ bonds and more Ge-H and CC bonds than the films deposited at the lower bias. Reduced incorporation of Ge-CH₃ fragments in the films results in denser films deposited at -250 V, as discussed above.

FTIR spectra of as-deposited a-GeC(O):H films are illustrated in Figure 6 for films deposited at biases of -150 V and -250 V, at the flow rate ratio $\text{O}_2/\text{TMGe} = 3$. The two spectra are similar having very small absorption peaks from C-H and Ge-H bonds, a large O-H absorption band at around 3400 cm^{-1} and strong absorption peak at 830 cm^{-1} . In order to obtain a clear assignment of the peaks in the absorption band between 900 and 720 cm^{-1} the band obtained for films deposited at different O_2/TMGe ratios was deconvoluted into two peaks centered at 830 and 780 cm^{-1} . The spectra of the various films was first normalized to a common 1 μm thickness, so that the area of the deconvoluted peaks could be compared between samples. The results showed that the area of the peak at 830 cm^{-1} increases with increasing O_2/TMGe ratio, whereas the area of the peak at 780 cm^{-1} stays essentially constant. Because increasing the oxygen concentration in the plasma causes an increased formation of GeO bonds, the 830 cm^{-1} peak whose intensity increases with increasing oxygen incorporation can be assigned to the Ge-O bond. The peak at 780 cm^{-1} whose area is not affected by the addition of oxygen at a constant bias, or power corresponds to the absorption of Ge-CH₃ bonds.¹⁰

An additional small and narrow peak is observed at 2340 cm^{-1} in the spectra of the a-GeC:H films deposited from a mixture with $\text{O}_2/\text{TMGe} \geq 3$. This peak shows the presence of CO₂ chemisorbed in the film indicating that, with sufficient O₂ addition to the plasma, CO₂ is formed and is incorporated in the films.

The FTIR spectra of as-deposited films prepared from TMGe+H₂ are similar to those of films prepared from pure TMGe films deposited at the same biases. However, the Ge-H and the

Ge-C-C peaks are bigger and the Ge-CH₃ peaks are smaller in the films prepared from TMGe+H₂. This indicates a stronger dissociation of the TMGe in the plasma, since formation of Ge-H and Ge-C-C bonds requires the dissociation of the Ge-C bond of TMGe. This dissociation can be enhanced by radical-molecule or radical-radical reactions¹¹, such as



which leads to the formation of the volatile CH₄ which is pumped out from the reactor. The reaction thus results in a reduced incorporation of Ge-CH₃ bonds and parallel increase in Ge-H bonds in the films.

The FTIR spectra of the films deposited from TMGe+Ar are similar to those of the films deposited from TMGe+H₂, the films containing more Ge-H and Ge-C-C bonds and less Ge-CH₃ bonds than the films deposited from pure TMGe. These changes in bond concentration indicate that the argon increases the dissociation of the species in the TMGe plasma through ion-molecule reactions.¹¹

III.b. Film stability

The stability of the films was characterized by studying the evolution of their optical properties over time. The index of refraction and the extinction coefficients of all investigated films did not change significantly with time, however the optical gap underwent changes which depended on the deposition conditions. The films deposited from pure TMGe at -250 V were characterized by an optical gap of 1.82 eV which did not change with time. However the optical gap of the films deposited at -150 V changed with time, increasing by 20 % after one month in air, as illustrated in Figure 7 for a film deposited from pure TMGe. The figure shows that the changes are faster in the first days, then decrease asymptotically with time. In the following we shall discuss the total changes between the as-deposited values and the asymptotic one.

The changes in the values of the optical gap are presented in Figure 8 for all investigated films deposited at a bias of -150V as a function of the concentration of the additive in the gas feed. The results show that the change in the optical gap decreases, i.e. the film stability improves, with increasing O₂/TMGe. Because a 5% change in the optical gap is within the experimental measurement error, it can be seen that for O₂/TMGe ratios higher than 3, the films can be considered practically stable. The films deposited at -150 V at a ratio O₂/TMGe = 6 or 10 showed no change in the optical gap over time, thus appearing to be perfectly stable. This is further confirmed by the change of the area of the FTIR Ge-O peak after 3 weeks, discussed later and shown in Table III. These results indicate that the instability of the a-GeCO:H films deposited at the lower bias is reduced by increasing the amount of oxygen in the plasma and full stability is reached at flow rate ratios of O₂/TMGe>3.

The addition of H₂ or Ar to TMGe had no effect on the stability of the films deposited at -250V, which were already stable without the precursor additives. The two additives do affect however the stability of the films deposited at -150V and both H₂ and Ar reduce the total changes in the optical gap. However, as shown in Figure 8, the optical gap still changes by more than 12% even for a flow ratio H₂/TMGe=3. While the films deposited from pure TMGe reached their final equilibrium optical gap after one month, the films deposited with addition of H₂ reached the equilibrium values in about 10 days and the films deposited with addition of Ar reached them after only a few days.

The stability of the a-GeC:H films was also evaluated from the changes in their FTIR spectra over time. The FTIR spectra of the films deposited from pure TMGe or from TMGe with additives at -250 V did not change over time, showing that these films have also a structural stability. However this is not true for the films deposited from pure TMGe at -150V. The FTIR spectrum of a film deposited from pure TMGe at -150 V after one month in air is superposed on the spectrum of the as-deposited film in Figure 9. It can be seen that the bonding in the film undergoes a drastic transformation with time. New absorption peaks appear at 3400 and 1690 cm⁻¹. These peaks are identified as belonging to O-H and carbonyl bonds (see Table II). The other peaks decrease or remain constant, with the exception of the Ge-O peak (830 cm⁻¹), which increases. The apparition and growth of the FTIR peaks of the Ge-O and C=O bonds proves that the film is interacting with the atmosphere and both carbon and germanium become oxidized, as indicated by the apparition.

The changes in FTIR spectra can be used to assess the relative stability of the films. Specifically, the area of the Ge-O peak, calculated from a deconvolution of the peak located at 830 cm⁻¹, is a good parameter for this purpose. The data for the a-GeC:H films deposited at -150 V can be found in Table III for films deposited from pure TMGe and for films deposited from TMGe+O₂. The area of the Ge-O peak of the film deposited from pure TMGe increases by 247 % after 3 weeks. The change in the area of this peak for the films deposited with oxygen addition to the plasma decreases with increasing O₂/TMGe ratio, reaching very low values for ratios >1.5. The negative values in Table III are most probably the result of experimental errors.

IV. CONCLUSIONS

The stability of the a-GeC(O):H films deposited by PECVD from pure TMGe and from TMGe with O₂, H₂ or Ar additions has been studied, monitoring the changes over time of their optical properties. It was found that all films deposited at a substrate bias of -250 V DC were stable in air, but the stability of the films deposited at a lower bias of -150 V DC was depended on the precursor mixture used for their deposition.

The films prepared at -150 V DC from pure TMGe were unstable in air and their properties changed continuously over several weeks. Additions of H₂ or Ar to TMGe improved only slightly the stability of the films.

Oxygen addition to TMGe improved the stability of the films, the improvement increasing with increasing concentration of O₂ in the gas mixture. For flow rate ratios O₂/TMGe>3 the films deposited at -150 V DC became completely stable, however they changed from a-GeC:H to mostly carbon containing amorphous germanium oxide films.

The stability of the investigated films appears to be correlated to their density, the stability increasing with increasing film density. The latter could be increased either by increasing the substrate bias or by the addition of oxygen. The stable films are characterized by densities greater than 3 g.cm⁻³.

ACKNOWLEDGMENTS

The authors are thankful to David R. Medeiros for helpful discussions and advice and to Andrew Kellock from the Almaden Research center for RBS and FRES analyses of the films.

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Table I. Deposition conditions and optical properties of as-deposited films.

Gas mixture	X* / TMGe	Bias (-V)	n @633 nm	k @633 nm	E_{opt} (eV)
TMGe	0.0	150	1.95	0	2.60
TMGe	0.0	250	2.64	0.087	1.84
TMGe + O ₂	0.1	150	1.84	0	2.98
TMGe + O ₂	0.2	150	1.72	0	2.89
TMGe + O ₂	0.5	150	1.66	0	3.78
TMGe + O ₂	1.0	150	1.68	0	3.75
TMGe + O ₂	1.0	250	2.06	0	2.75
TMGe + O ₂	1.5	150	1.68	0	3.96
TMGe + O ₂	3.0	150	1.70	0	3.77
TMGe + O ₂	3.0	250	1.76	0	2.76
TMGe + O ₂	6.0	150	1.71	0	4.00
TMGe + O ₂	6.0	250	1.69	0	4.02
TMGe + O ₂	10.0	150	1.65	0	4.38
TMGe + O ₂	10.0	250	1.61	0	4.64
TMGe + H ₂	0.5	150	1.96	0.001	2.54
TMGe + H ₂	1.5	150	2.04	0.021	2.28
TMGe + H ₂	1.5	250	2.68	0.139	1.69
TMGe + H ₂	3.0	150	2.21	0.030	2.09
TMGe + Ar	0.5	150	2.01	0.004	2.43
TMGe + Ar	2.0	150	2.02	0.007	2.42

*) X=O₂, H₂, or Ar

Table II. Identification of FTIR peaks of a-GeC(O):H films.

Wavenumber (cm ⁻¹)	Peak Assignment	Reference No.
3400	-OH polymeric; intermolecular H-bond	[9,15]
2970	sp ³ CH ₃ as* stretch	[9,10]
	sp ² CH ₂ sym* stretch	[9]
2910	sp ³ CH ₂ as stretch	[9,13]
	-CH ₃ sym stretch or -CH ₂ stretch	[10]
2870	sp ³ CH ₃ sym stretch	[9]
	CH ₂ ** sym stretch	[10]
2340	CO ₂ chemisorbed	
2120 - 1990	Ge-H and Ge-H ₂	[3]
	Ge-H stretch	[9]
1795	aromatics	[10]
1715	-C=O	[10]
1680	C=C stretch (O-C=C)	[10]
1570	sp ² C=C, aromatics	[9,10]
1455	sp ³ CH ₃ as bend	[9,10]
1412	sp ² CH bend in RRC=CH ₂ , RCH=CH ₂ or RCH=CHR	[9]
	-CH ₂ -CO-	[9]
	Ge-CH ₂ -Ge	[6]
1365	sp ³ CH ₃ sym bend	[9,10]
1230	Ge-CH ₃	[10]
	epoxy (8 μ band)	[9]
	CH ₂ ** bent sym	[10]
1140	(CH ₃) ₂ -CH-	[9]
1110	Ge-C-C stretch	[10]
1040 - 980	C-C stretch	[10]
	sp ² C=C, olefinic	[10]
	sp ² CH	[9]
830 - 810	Ge-O	[10]
780	Ge-CH ₃ rock, Ge-H bend	[3]
700	sp ¹ CH, sp ² CH ₂ , sp ³ CH ₂	[12]
	CH ₂ ** rocking	[10]
630	Ge-(CH ₂) ₄ stretch	[1,3]
580	Ge-H wagging, C-Ge-C as stretch	[3]

* sym: symmetric; as: asymmetric

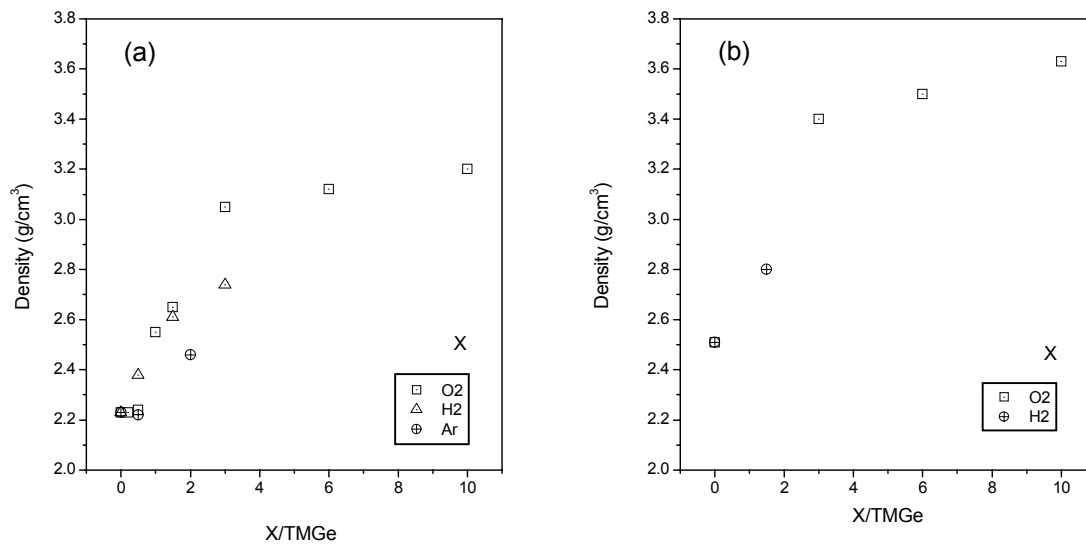
** hybridation not mentioned

Table III. Areas of the deconvoluted Ge-O peak at 830 cm^{-1} of a-GeCO:H films deposited at -150 V, and their change with age.

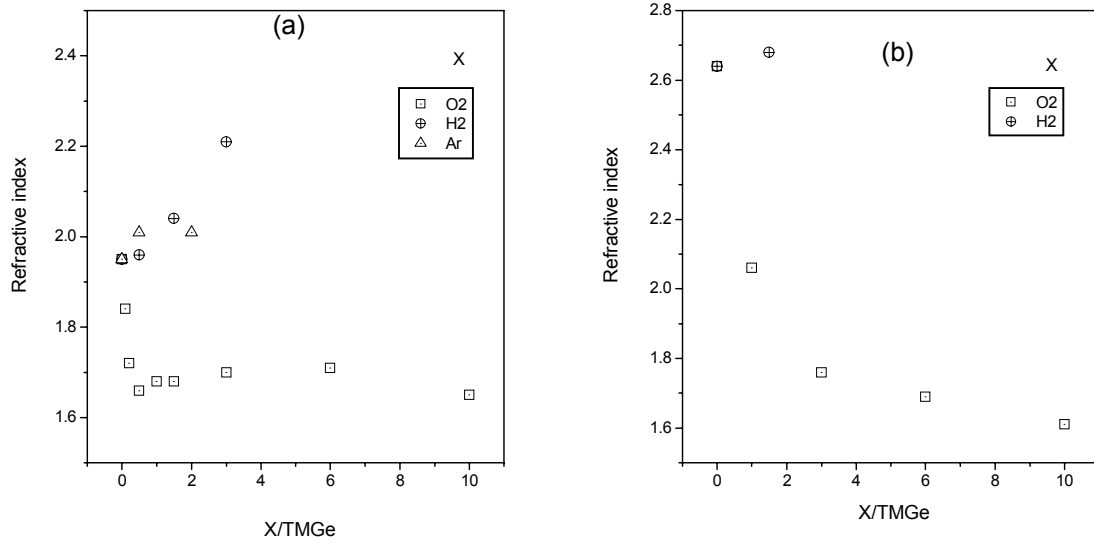
O₂ / TMGe	Area as-deposited	Area after 3 weeks	Area increase (%) after 3 weeks
0.0	2.1	7.4	247
0.5	9.1	13.2	45
1.0	10.8	13.4	25
1.5	13.8	14.4	4
3.0	24.0	21.0	-13
10.0	45.5	45.0	-1

Figure Captions

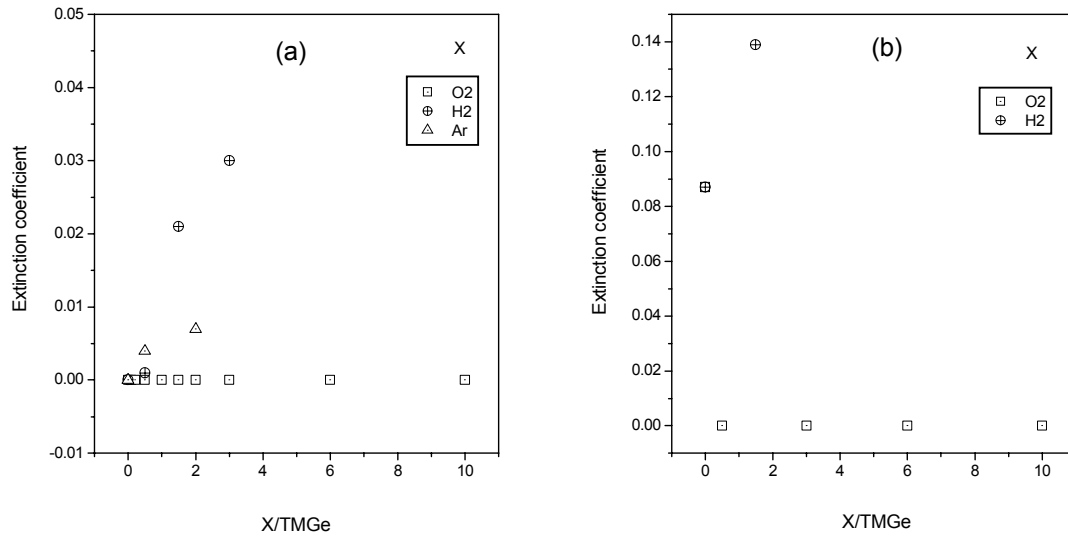
- Figure 1. Density of a-GeC(O):H films as a function of the precursor mixture. a) deposited at a bias of -150V; b) deposited at a bias of -250V.
- Figure 2. Refractive indexes of a-GeC(O):H films as a function of the precursor mixture. a) deposited at a bias of -150V; b) deposited at a bias of -250V.
- Figure 3. Extinction coefficients of a-GeC(O):H films as a function of the precursor mixture. a) deposited at a bias of -150V; b) deposited at a bias of -250V.
- Figure 4. Optical gap of a-GeC(O):H films as a function of the precursor mixture. a) deposited at a bias of -150V; b) deposited at a bias of -250V.
- Figure 5. FTIR spectra of as deposited a-GeC:H films deposited from pure TMGe. a) deposited at -150 V; b) deposited at -250 V.
- Figure 6. FTIR spectra of films deposited from TMGe+O₂ at a flow rate ratio O₂/TMGe=3. a) deposited at a bias of -150V; b) deposited at a bias of -250V.
- Figure 7. The optical gap of an a-GeC:H film deposited at -150 V as a function of time.
- Figure 8. Total changes in the values of the optical gap of a-GeC(O):H films film deposited at -150 V.
- Figure 9. FTIR spectra of a-GeC:H films deposited from TMGe at -150 V, as-deposited and after one month in air.



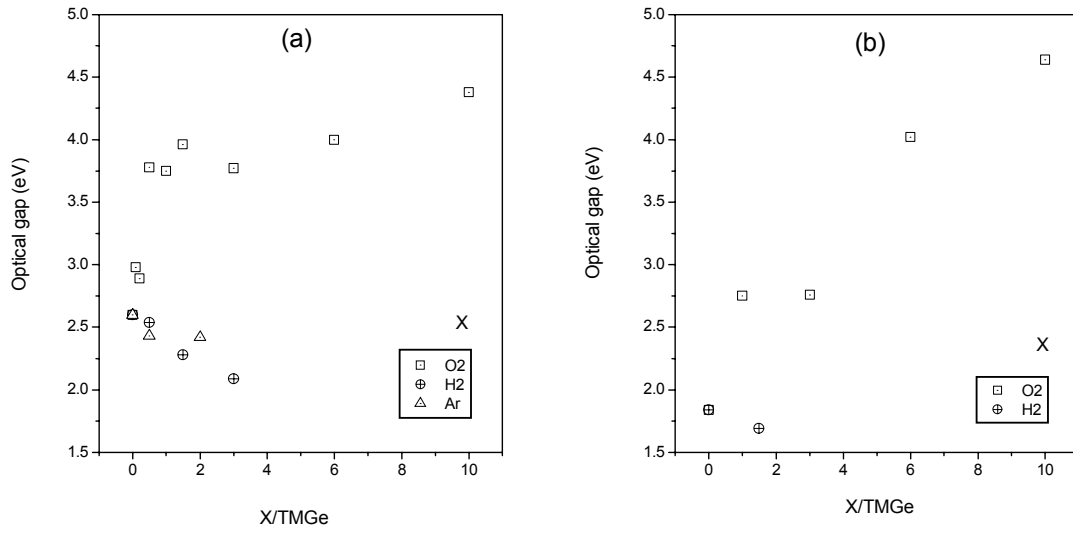
A. Grill - Figure 1



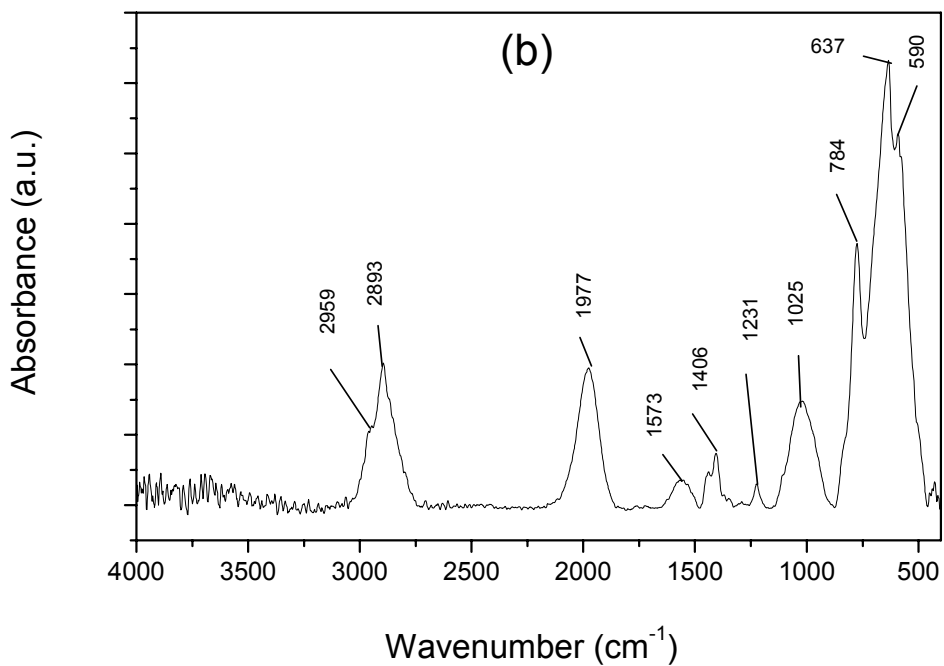
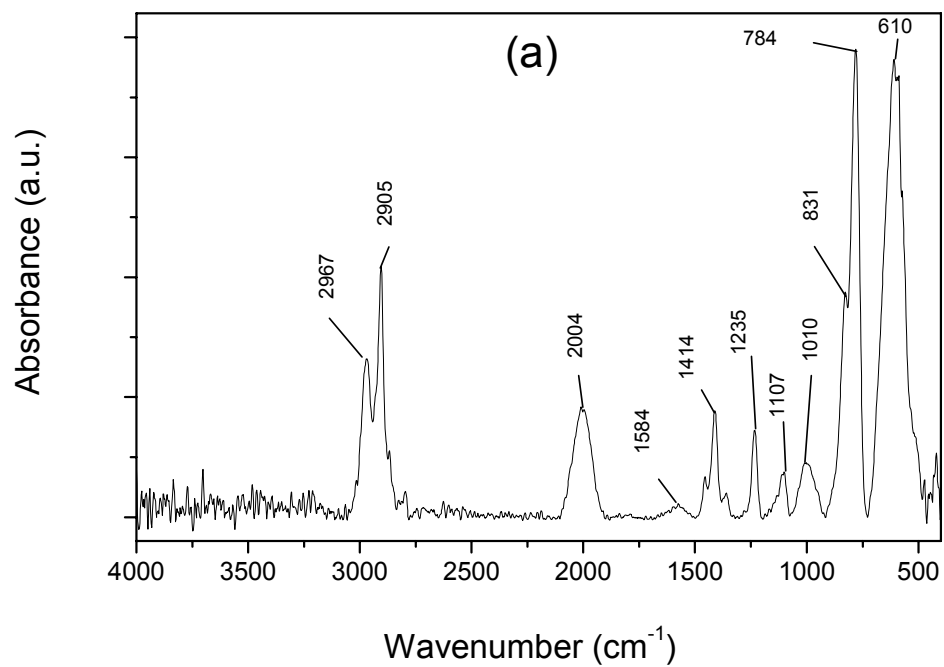
A. Grill - Figure 2



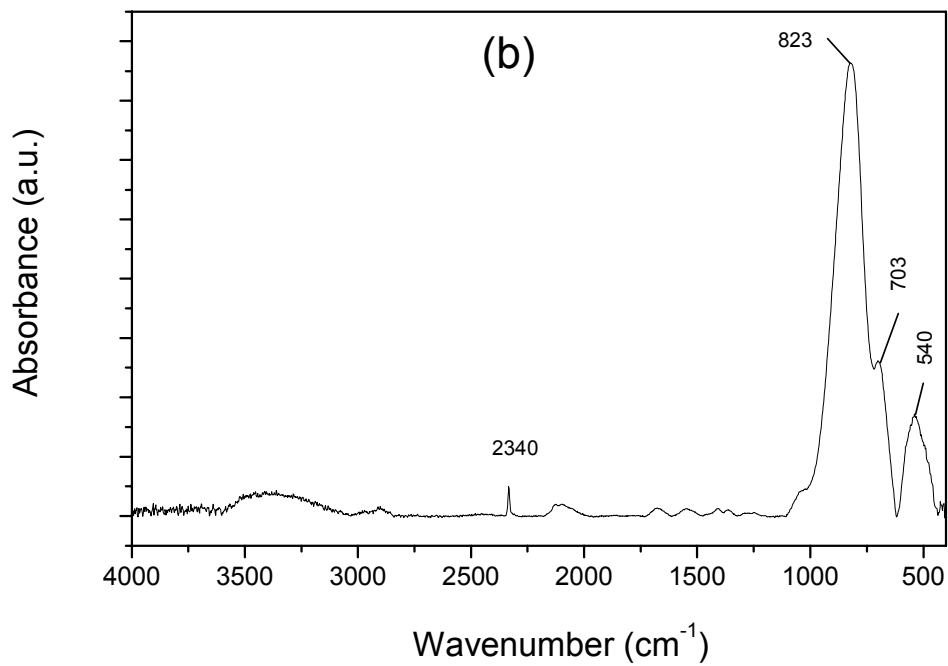
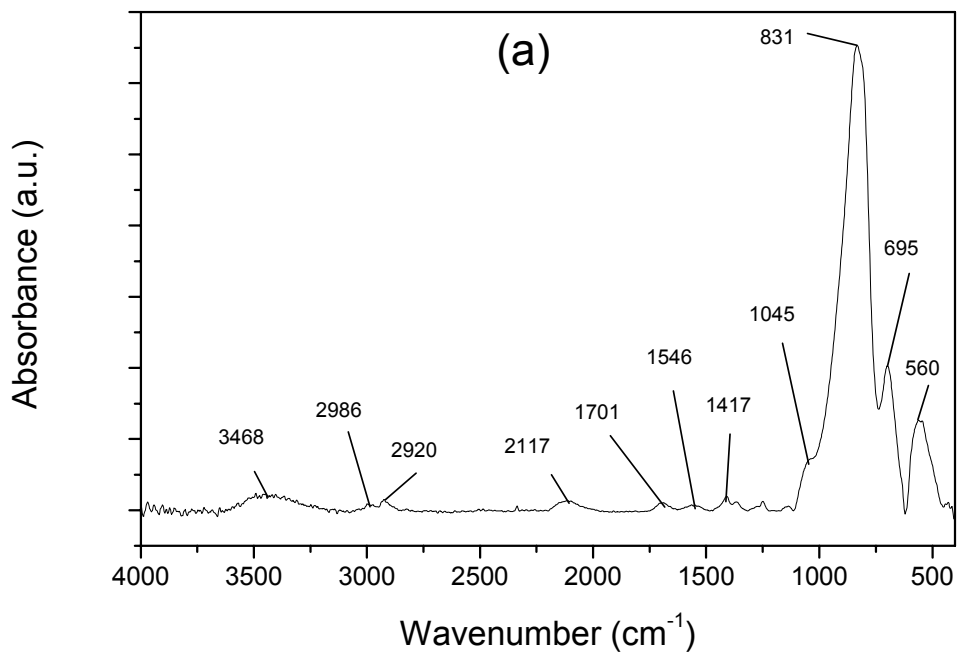
A. Grill - Figure 3



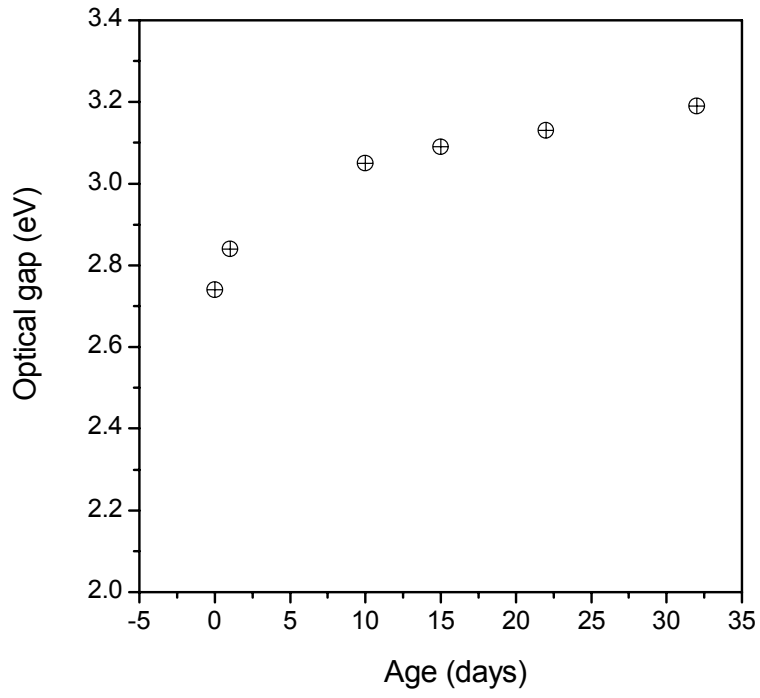
A. Grill - Figure 4



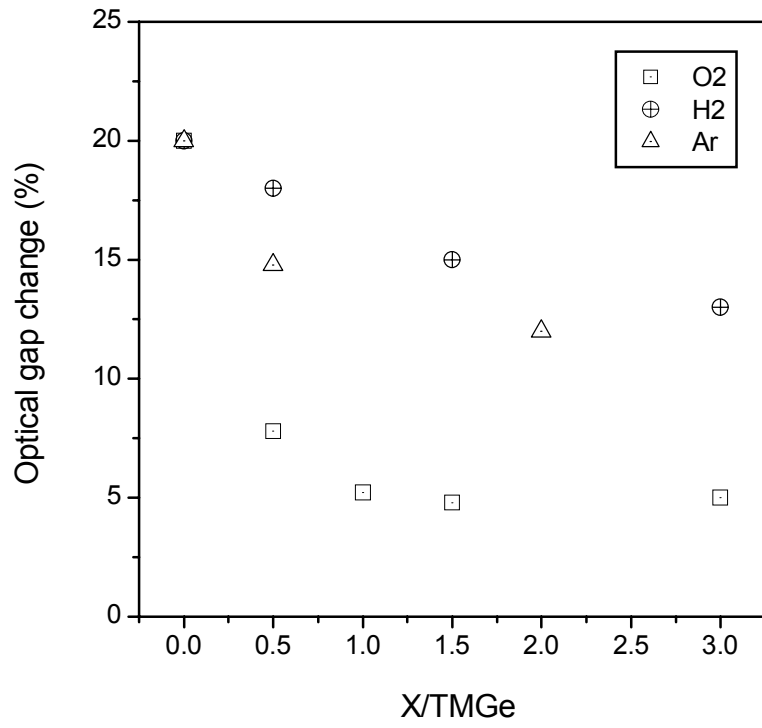
A. Grill - Figure 5



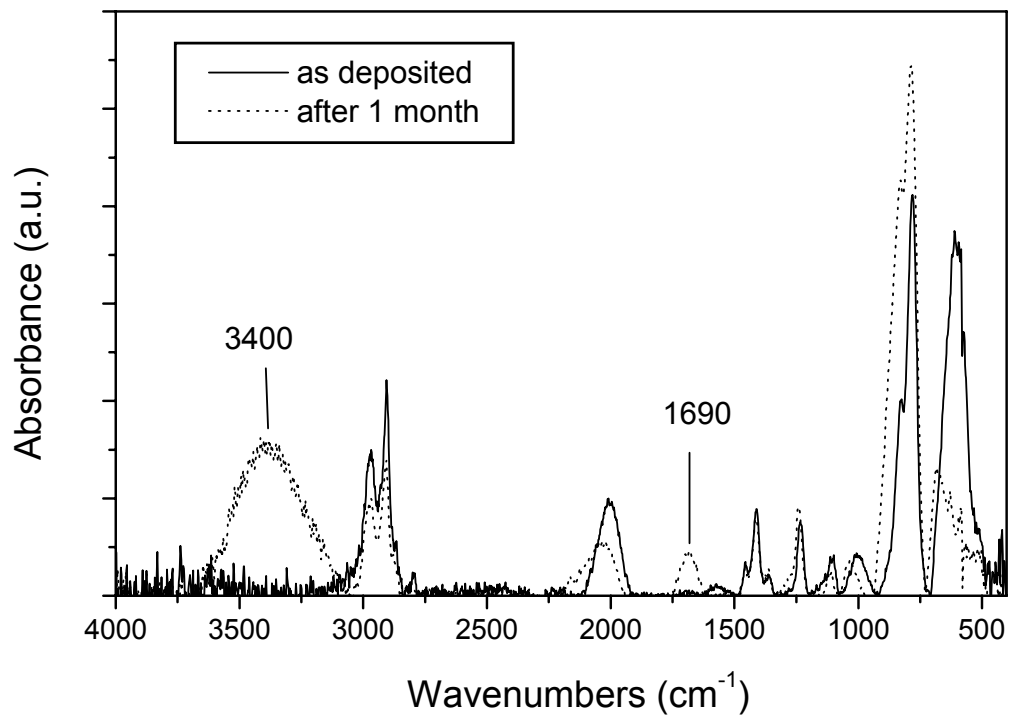
A. Grill - Figure 6



A. Grill - Figure 7



A. Grill - Figure 8



A. Grill - Figure 9