AN INVESTIGATION OF GERMANIUM COATED BLACK KAPTON AND UPILEX FILMS UNDER DIFFERENT ENVIRONMENTAL GROUND CONDITIONS

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ABSTRACT

Recently, blotch-like darkening on Germanium coated polyimide films was found after apparent storage in a controlled cleanroom environment. Whereas the limited stability of Germanium coatings in air is generally recognized, the severity of the degradation within a relatively short time frame triggered this investigation on the long-duration stability of Germanium coatings. Three different Germanium coated polyimide films, black Kapton, Upilex S and Upilex S/VDA, have been studied under different storage conditions with controlled temperature, humidity level, and oxygen content over a period of one year. Evidently, increasing relative humidity as well as temperature accelerated the Germanium degradation process. In order to understand the degradation of Germanium under these conditions, several measurements have been performed at the beginning of the test, at some inspection points and at the end of the test campaign. Visual inspections, thermo-optical measurements, Scanning Electron Microscopy (SEM) and Kelvin probe measurements were performed.

1. INTRODUCTION

Germanium coated polyimide films are commonly used on the RF/microwave antennae sunshields to protect them from solar radiation. With a surface resistivity of $\sim 10^8$ Ω/square and a low absorptance, Germanium provides ESD protection and thermal control [1]. Among various types of polyimide films, black Kapton-type and Upilex-S type polyimide films offer very good mechanical, thermal, and optical properties.

However, during storage, even under standard cleanroom conditions, Germanium coated black Kapton and Upilex S can undergo significant degradation on the metallic surface affecting the properties of the films. Therefore, the objective of this activity was to investigate the degradation of germanium coated films under the influence of standard and accelerated storage conditions. Film surfaces exposed to different storage conditions were characterized by thermo-optical, Kelvin probe and Scanning Electron Microscopy measurements at several inspection points over one year.

2. SAMPLE DESCRIPTION

Three types of Germanium coated polyimide samples were chosen: Ge/black Kapton, Ge/UpilexS and third sample was Ge/UpilexS coated from opposite to germanium coating by vapour deposited aluminium (see Table 1). The polyimide film was about 25 µm. Forty nine square samples with a surface of 50x50 mm^2 were cut and prepared for this investigation.

Table 1 Sample description

Sample designation	Polyimide film		Coating	
	Type	*Thickness*	*Front*	*Back*
Ge/black Kapton	Black Kapton	25 µm	Ge	-
Ge/UpilexS	UpilexS		Ge	-
Ge/UpilexS/ VDA	UpilexS		Ge	Al

The films were conditioned in five different storage desiccators in which the relative humidity (0%, 58% and 97%) and temperature were controlled. In order to reach the relative humidity (RH) level required in desiccators A, B, C and D, each desiccator was containing salt baths: potassiumsulfate salt for 97% RH, sodium bromide for 58% RH and silica gel for 0% RH. The nominal conditions are summarized in Table 2.

Desiccators A, B, D and E were filled in with air and only desiccator C was under nitrogen environment. Desiccators A, B, C and D were all at room temperature (RT), but the relative humidity was varying from dry air (desiccator D), to 58% RH (desiccator A) to 97% RH (desiccator B). A second investigation has been carried out on Germanium coated polyimide films in normal air at higher temperature, 50 ºC, and 97% RH for one month in desiccator E.

Table 2 Nominal conditions

Desiccator	Gas environment	T (ºC)	RH (%)
A	Air	25 *(18 – 25.5)**	58 *(53 – 63)**
B	Air	25 *(17.5 – 25.5)**	97 *(86 – 100)**
C	Nitrogen	25 *(18.5 – 25)**	0 *(2 – 37)**
D	Air	25 *(18 – 25)**	0 *(13.5 – 36)**
E	Air	50	97

*In brackets are shown the measured conditions after one year testing

3. EXPERIMENTAL METHODS

Three types of characterisation have been performed in order to get a better understanding on the degradation effects: thermo-optical characterisation (absorptivity, emissivity), Kelvin probe characterisation and SEM combined with Energy Disperse X-Ray Spectroscopy (EDX) characterisation.

3.1 Thermo-optical measurements

The solar reflectance was determined over the wavelength range λ_1 = 250 nm to λ_2 = 2500 nm using the Cary 500 (UV/VIS/NIR) spectrophotometer with an integrating sphere (DRA). From the reflectance spectra, the solar absorptance (α_s) was calculated by weighing the measured reflectance spectrum with the solar spectrum. The weighed spectrum was resulting in the solar reflectance (Equation 1). The solar absorptance was the complementary value (Equation 2).

$$R_s = \frac{\int_{\lambda_1}^{\lambda_2} R_\lambda S_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} S_\lambda d\lambda} \quad (1)$$

$$\alpha_s = 1 - R_s \quad (2)$$

The thermal emittance ε_N was determined using the AZ-TEK TEMP 2000A equipment. The sample was placed against the aperture of the device and was irradiated by infrared radiation. The signal obtained was integrated over the spectral range from 3µm to over 30µm and weighed by the spectrum of a 300K blackbody. Both measurements were performed according to ECSS-Q-70-09 [2].

3.2 Kelvin probe measurements

A Scanning Kelvin probe system SKP5050 was used to measure the work function of Germanium coated black Kapton and Upilex S by placing a 0.5 mm vibrating stainless steel reference tip (69 Hz) above the sample electrode. The probe was measuring the difference in the work function between the reference material and the sample surface.

A calibration with pure gold and pure aluminium was first performed as their work function was well known. Samples to investigate were then attached to a SEM stub. The surface of the samples was grounded by using conductive silver glue and placed into a relative humidity chamber RHC020. The chamber was controlled by a RH unit with humidifier and dehumidifier at a range from 10 to 100%. A computer with a data acquisition system was used to control the instrument and to collect measured data.

3.3 SEM/EDX measurements

Imaging the top surface of Germanium films was performed using the SEM LEO 1530VP microscope operating at 10 kV. Elemental composition analysis was carried out by EDX spectroscopy. The specimens for SEM/EDX analysis were fixed to aluminium stubs by carbon tape and placed in the equipment under vacuum. They were observed at different magnifications.

4. RESULTS AND DISCUSSION

All the measurements were performed at the beginning of the test campaign, after several inspection points (1 week, 2 weeks, 1 month, 2 month, 4 month and 9 month) and at the end of the test campaign after 12 month.

4.1 Visual inspection

Visual appearance of the samples is shown on Figs 1, 2 and 3. In dry conditions under air or nitrogen, no visual degradation has been observed on the samples. However, when the relative humidity reaches 58%, few small size spots start to appear on the germanium surfaces. They grow faster when the relative humidity is increasing till 97% and the temperature rises from room temperature to 50ºC. The spots are spread all over the germanium surface and the edges of the samples seem to be first affected.

At 58% RH, no clear distinction can be made between the different germanium coatings (see Fig.1). As the humidity is rising, a more significant degradation occurs on Ge/UpilexS and Ge/black Kapton samples

than on Ge/UpilexS/VDA (see Fig. 2). The backing aluminium layer of Ge/UpilexS/VDA sample prevents from observing the severity of degradation of the germanium surface.

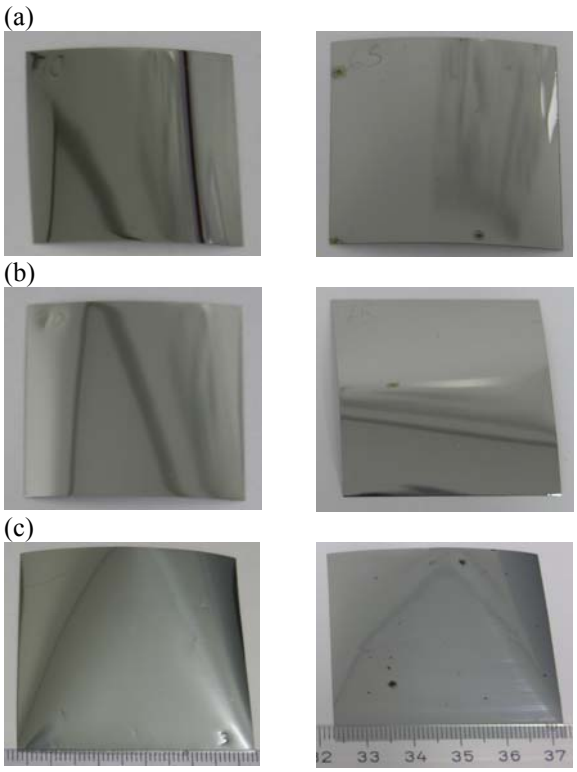

Figure 1 Optical images of (a) Ge/UpilexS sample; (b) Ge/UpilexS/VDA sample and (c) Ge/black Kapton sample in the desiccator A (58% RH). Left pictures have been taken after 2 month testing and right pictures have been taken after one year testing.

Increasing the temperature is causing even more serious degradation over a very short time as larger areas of polymer film remain uncovered by germanium coating. Ge/UpilexS and Ge/black Kapton samples seem again to degrade more than Ge/UpilexS/VDA sample (see Fig.3).

When considering the spots size and their repartition over the germanium surface, it has been shown that:

- About 2 month testing performed at RT and 97% RH leads to a similar visual degradation of Ge/black Kapton after one year testing under cleanroom conditions (RT/58% RH). If the temperature is rising till 50ºC, only less than 1 week testing performed at 50ºC and 97% RH shows a similar degradation of the sample after one year under cleanroom conditions.
- About 4 month testing performed at RT and 97% RH leads to a similar visual degradation of Ge/UpilexS after one year testing under cleanroom conditions (RT/58% RH). If the temperature is rising till 50ºC, only less than 1 week testing performed at 50ºC and 97% RH shows a similar degradation of the sample after one year under cleanroom conditions.
- Less than 9 month testing performed at RT and 97% RH leads to a similar visual degradation of Ge/UpilexS/VDA after one year testing under cleanroom conditions (RT/58% RH). If the temperature is rising till 50ºC, about 2 weeks at 50ºC and 97% RH shows a similar degradation of the sample after one year under cleanroom conditions.

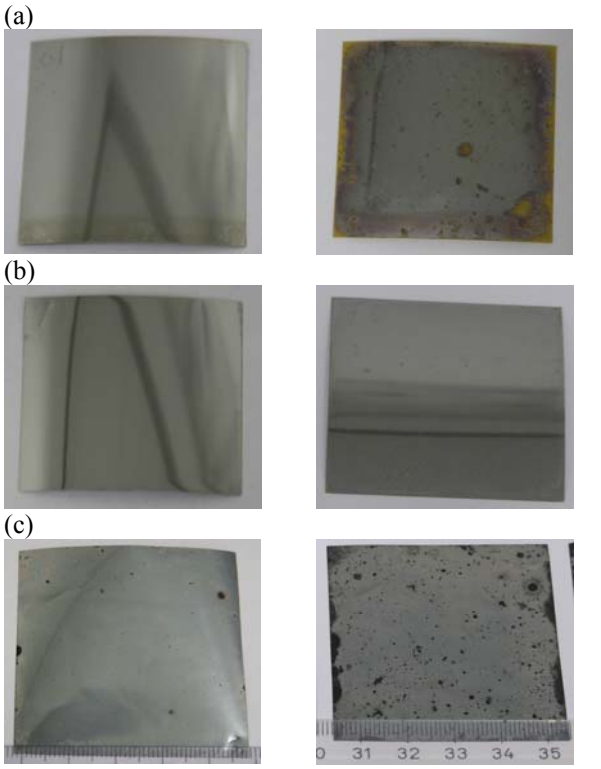

Figure 2 Optical images of (a) Ge/UpilexS sample; (b) Ge/UpilexS/VDA sample and (c) Ge/black Kapton sample in the desiccator B (97% RH). Left pictures have been taken after 2 month testing and right pictures have been taken after one year testing.

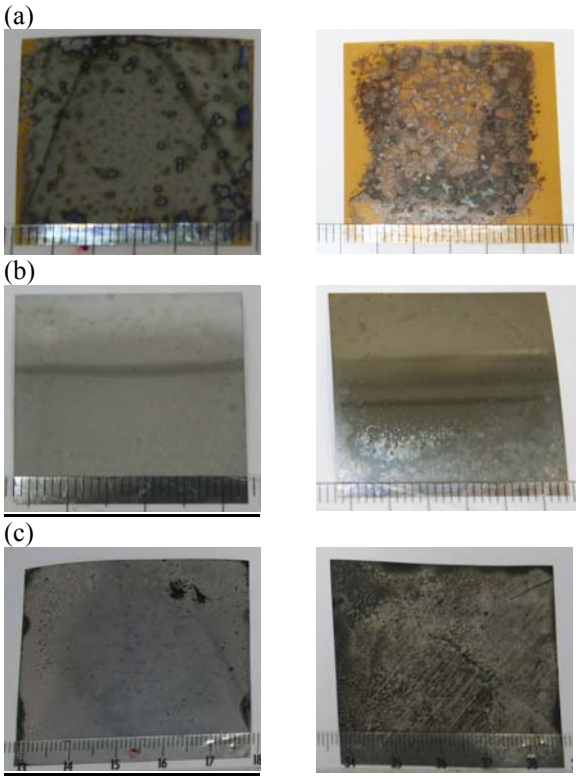

Figure 3 Optical images of (a) Ge/UpilexS sample; (b) Ge/UpilexS/VDA sample and (c) Ge/black Kapton sample in the desiccator E (97% RH and 50°C). Left pictures have been taken after 2 weeks testing and right pictures have been taken after 1 month testing.

4.2 Thermo-optical results

4.2.1 Solar absorptance values

The solar absorptance evolution of Germanium coated polyimide films in desiccators A and B is shown on Fig.4 and Fig.5.

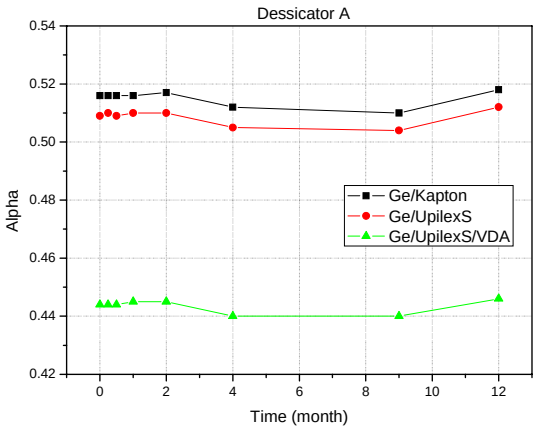

Figure 4 Alpha evolution of Ge coated polyimide films in desiccator A (RT/58% RH)

Ge coated Kapton and Ge coated Upilex S present initial absorptance values of 0.52 and 0.51 respectively. Ge coated UpilexS/VDA seems slightly more reflective with an absorptance value of 0.44. Samples in desiccator A remain quite stable after one year testing. The change in alpha is less than 0.5% at the end of the campaign. The samples placed in desiccators C and D indicate a similar behaviour.

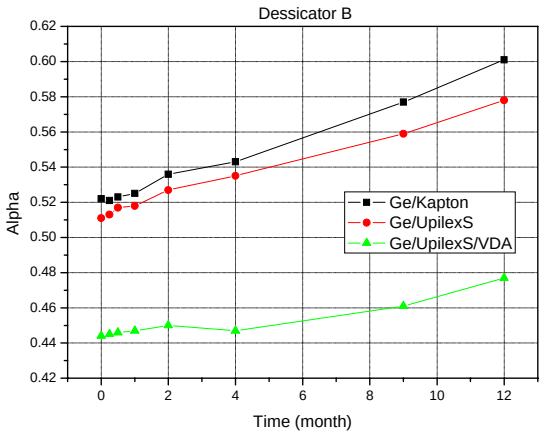

Figure 5 Alpha evolution of Ge coated polyimide films in desiccator B (RT/97% RH)

However, it can be seen on Fig. 5 that under very high humidity, Germanium samples degrade significantly and show an increase of the absorptance values by 15% for Ge/black Kapton, 13% for Ge/UpilexS and 8% for Ge/UpilexS/VDA after one year.

4.2.2 Thermal emittance values

Fig. 6 indicates the normal emissivity results of the Ge coated polyimide films at the beginning of the test and after one year.

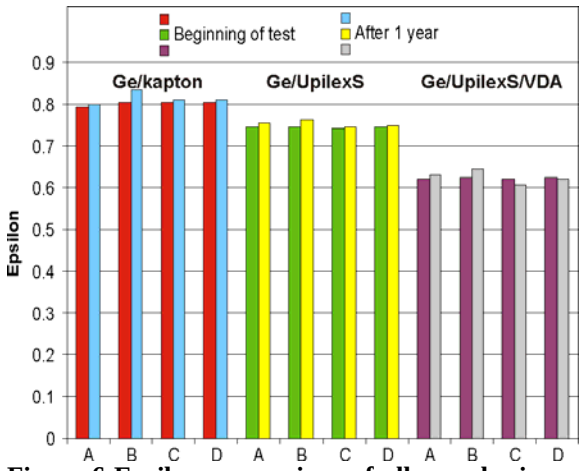

Figure 6 Epsilon comparison of all samples in each desiccator

They all present initially high values: 0.8 for Ge/black Kapton, 0.75 for Ge/UpilexS and 0.6 for Ge/UpilexS/VDA. No significant change in emissivity can be observed for the three types of Ge coatings (maximum increase of 4% for samples under highest humidity) after one year.

4.2.3 Ratio values

Based on the solar absorptance and normal emissivity results, the ratio α/ε of the samples was obtained.

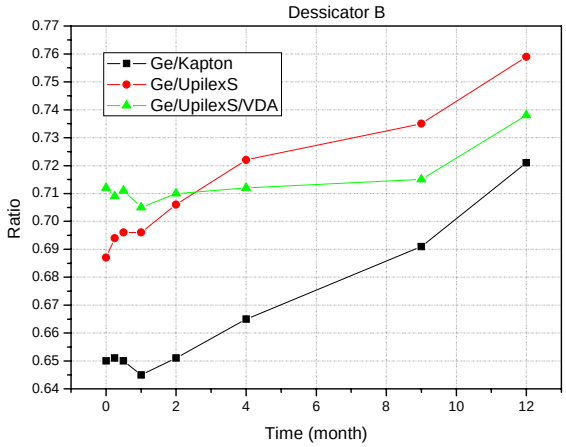

Figure 7 Ratio evolution of Ge coated polyimide films in desiccator B (97% RH)

Samples in desiccator B show an optical reflective degradation after one year as their α/ε ratios increase by 11% for Ge/black Kapton, 10% for Ge/UpilexS and 3% for Ge/UpilexS/VDA. This significant increase is not observed in desiccators A, C and D.

The temperature is also playing a role in the degradation process of the Germanium coatings as the second investigation carried out at 50ºC and 97% RH has revealed an acceleration of the degradation of the films (see Fig. 7). Indeed, after one month under high temperature, the ratio values increase by 28% for Ge/black Kapton and 12% for Ge/UpilexS. Only Ge/UpilexS/VDA stays stable as no thermo-optical change was observed, which has been confirmed by the absence of darker spots on the germanium surfaces during visual inspection (see Fig. 2b).

Increasing relative humidity and temperature is definitively affecting germanium surfaces in a very short time. The thermo-optical properties of the germanium films are more degraded after one month under 50ºC and 97% RH than after one year under cleanroom conditions (see Figs. 8, 9 and 10).

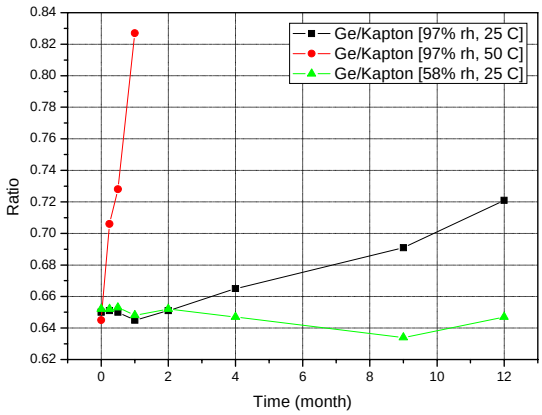

Figure 8 Ratio evolution of Ge/black Kapton sample in desiccators A (RT/58% RH), B (RT/97% RH) and E (50ºC/97% RH) over 1 year

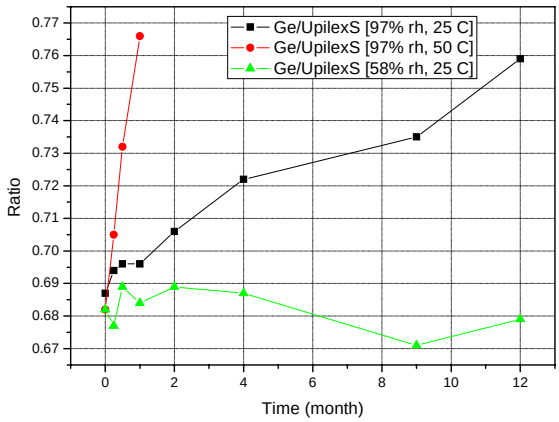

Figure 9 Ratio evolution of Ge/UpilexS sample in desiccators A (RT/58% RH), B (RT/97% RH) and E (50ºC/97% RH) over 1 year

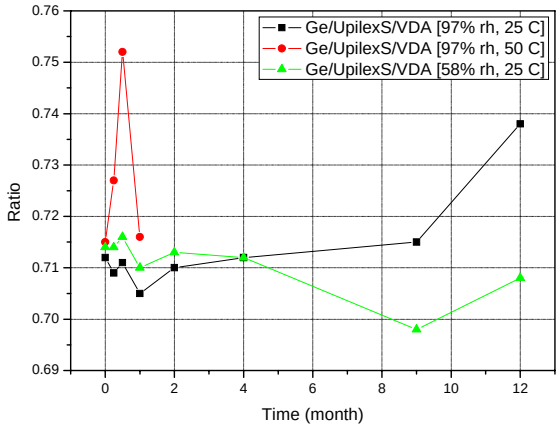

Figure 10 Ratio evolution of Ge/UpilexS/VDA sample in desiccators A (RT/58% RH), B (RT/97% RH) and E (50ºC/97% RH) over 1 year

We can clearly observe that Ge/black Kapton is degrading much faster than Ge/UpilexS and Ge/UpilexS/VDA. For the Ge/black Kapton sample, as seen before (paragraph 4.1), the test performed at RT and 97% RH accelerates 6 times more the degradation of the sample than under normal cleanroom conditions. If the temperature is rising till 50ºC, the acceleration factor is even higher than 12.

4.3 Kelvin probe results

In order to understand the degradation of two different Germanium coated polyimide films (black Kapton and Upilex) Kelvin work function measurements were performed while relative humidity level was varying from 55 to 97%.

Fig. 11 indicates the work function evolution of the samples depending on the relative humidity. The work function of the calibration sample aluminium on kapton seems quite stable (-800 mV) when the humidity is increasing. The work function of the gold on kapton calibration sample is decreasing slightly to zero at very high humidity levels.

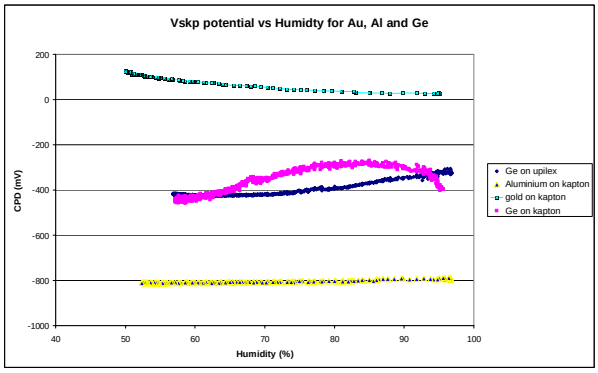

Figure 11 Work function evolution of calibration samples of Gold on Kapton, Aluminium on Kapton, Germanium coated black Kapton and Germanium coated Upilex S vs humidity

During the corrosion process, Germanium coated polyimide films start to degrade but show a clear difference in their work function at high humidity levels. Indeed, the work function of Ge/UpilexS is increasing from -425 mV to -300 mV when the relative humidity is rising from 55% to 97%. A faster increase is observed for Ge/black Kapton from -450 mV to -300 mV until 80% RH. However, from 80 to 97%, its behaviour changes drastically as its work function starts to decrease.

Since the work function depends mainly on the surface state of the material layer [3], the coating polymer layer shouldnot influence the work function of both Germanium coated polyimide films. The behaviour difference observed could be due to the germanium layer which can differ between both samples. Indeed, during visual inspection, we have noticed that Ge/UpilexS was shinier than Ge/black Kapton.

Furthermore, when exposed to humidity, additional layers of absorbed or evaporated water can be formed on the metallic surface, including oxide layer imperfections, surface and bulk contamination and surface charging. These layers contain charged species together with induced dipoles from dipolar molecules or polarized atoms, which can influence the work function of the material [4].

Understanding the fundamental effects that could cause the difference in the work functions requires a deeper investigation. It may be possible to develop a method that enables fast response on the oxidation stability of Ge-coatings.

4.4 SEM/EDX results

Surface morphology and chemical composition of Ge coated poylimide films were identified using SEM technique combined with EDX analysis. Results of SEM analysis of surfaces of initial films of germanium coated black Kapton and Upilex S samples show that germanium coating forms uniform and smooth layers on surfaces of polymer films; no large defects are detected (SEM images are not presented). EDX analysis reveals presence of germanium and trace of oxygen in some places.

Fig. 12 presents SEM images of germanium coated Kapton and Upilex S placed in the desiccator B after nine month of testing. One can see a significant degradation of the germanium coating: formation of large conglomerates of particles surrounded by darker areas. EDX analysis reveals that these particles consist from germanium (67±1% atomic percent) and oxygen (33±1% atomic percent), which denotes on the oxidation of germanium. Areas around particles contain mainly carbon indicating on vanishing of the germanium coating in these spots. Since such a degradation of germanium coatings occurs only in high humidity conditions, we believe that this process proceeds in several steps: (1) adsorption of water molecules on surfaces of germanium surfaces; (2) oxidation of germanium by adsorbed water; (3) formation of small particles of germanium oxide/hydroxide (up to 1 µm) and breaking of germanium coating due to its oxidation; (4) formation larger particles of germanium oxide/hydroxide (up to several tens of micrometres) through diffusion of small particles and their agglomeration. This agglomeration

leads to the reduction of particle surface energy and also results in uncovering of underlying polymer films which appear darker on SEM images and in areas around particles (see Fig. 12).

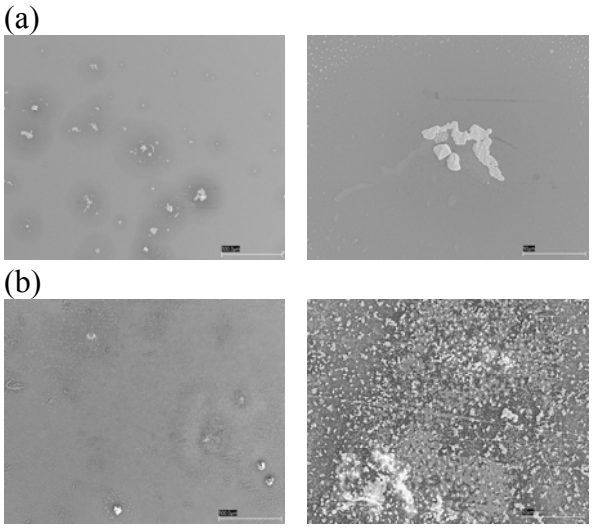

Figure 12 SEM image of (a) Ge/UpilexS sample; (b) Ge/black Kapton sample in the desiccator B after 9 month testing. Left pictures refer to a low magnification and right pictures to a high magnification image.

5. CONCLUSION

During storage time, it has been found that germanium suffers from corrosive degradation when exposed to humidity and temperature. Oxidation causes pitting of the germanium film and affects the thermo-optical properties of the Germanium. At 50ºC and 97% RH, the samples have shown large dark spots on the germanium surfaces resulting in uncovered areas of polymer film.

The process of degradation is supposed to occur in several steps: (1) adsorption of water molecules on germanium surfaces; (2) oxidation of germanium; (3) formation of small particles of germanium oxide/hydroxide; (4) agglomeration and creation of larger particles of germanium oxide/hydroxide.

The three samples investigated exhibited different behaviour, probably caused by a different germanium coating process depending on the manufacturer, not so much by the actual substrate. Several grades of germanium coatings could result in different qualities of germanium surfaces and therefore different storage stability. Possibly even batch variations may result in different behaviours. Since observable degradation did already occur after 1 year at 58% RH and RT, it is advised to store Ge-coated polyimide films under as dry conditions as possibly, ideally under N2 purge. Relative quick assessment of storage stability is possible using higher humidity and temperature. Considering the visual degradation, the acceleration was roughly factor 6 for Ge/black Kapton, factor 3 for Ge/UpilexS and factor 2 for Ge/UpilexS/VDA under 97%/RT conditions. The acceleration was higher than factor 12 for all samples under 97%/50°C.

6. REFERENCES

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