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Moisture barrier enhancement by spontaneous formation of silicon oxide interlayers in hot wire chemical vapor deposition of silicon nitride on poly(glycidyl methacrylate)¹

D.A. Spee, C.H.M. van der Werf, J.K. Rath, and R.E.I. Schropp

Abstract: We deposited a silicon nitride (SiN_x)-polymer hybrid multilayer moisture barrier in a hot wire chemical vapor deposition (HWCVD) process, entirely below 100 °C. The polymer, poly(glycidyl methacrylate) (PGMA), was deposited by initiated chemical vapour deposition and the SiN_x in a dedicated HWCVD reactor. Line profile investigation of our barrier structures by cross-sectional scanning transmission electron microscopy and energy dispersive X-ray spectrometry reveals that, upon deposition of SiN_x on top of our polymer layer, an intermediate layer of silicon oxide (SiO_x) like material is formed. X-ray photoelectron spectroscopy measurements confirm the presence of this material and indicate the epoxy rings in the PGMA material open upon heating (to 100 °C) and exposure to atomic hydrogen and amine species in the HWCVD process. The oxygen atoms subsequently react with silicon and nitrogen containing radicals to form SiO_xN_y . The interlayer turns out to be highly beneficial for interlayer adhesion and this is considered to be one of the reasons for the excellent barrier properties of our multilayer.

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Résumé : Nous déposons un pare-vapeur multicouche hybride de nitrure de silicium (SiN_x)/polymère par un procédé de dépôt de vapeur chimique due à un filament chaud (HWCVD), le tout sous les 100 °C. Le polymère, poly(méthacrylate de glycidyle) (PGMA), est déposé en vapeur chimique par activation et le SiN_x dans un réacteur HWCVD dédié. Nous analysons les profils de ligne de la structure de nos barrières à l'aide de la microscopie électronique en transmission, avec balayage de la section efficace et par analyse X dispersive en énergie. Cette analyse révèle qu'en déposant SiN_x sur le polymère, il se forme une couche intermédiaire de matériau de type SiO_x . Des mesures XPS confirment la présence de ce matériau et indiquent la présence de structures circulaires dans le PGMA lorsque chauffé à 100 °C et exposé à l'hydrogène atomique et à des amines durant le procédé HWCVD. Les atomes d'oxygène réagissent alors avec le Si et les radicaux N pour former du SiO_xN_y . Cette couche intermédiaire s'avère bénéfique pour l'adhésion entre les couches et est considérée comme une des raisons pour les excellentes propriétés de pare-vapeur de notre multicouche.

1. Introduction

Sensitive electronic devices can swiftly degrade because of oxygen and water vapor permeating into their active layers. For devices made on flexible plastic substrates, which, contrary to glass, have a high permeability to oxygen and water, this is an important issue. Hence, permeation barrier layers on flexible substrates are required for many devices, including organic light emitting diodes, flexible solar cells, and rollable displays [1–3]. Such a barrier can be created with an inorganic-organic multilayer, in which the organic layers decouple defects in consecutive inorganic layers. In this manner, chances of permeation paths like pinholes or cracks propagating through the entire multilayer are decreased. A combination of silicon nitride (SiN_x), which is deposited without using oxidative source gasses, and a polymer is very suitable to create such a multilayer [4]. We are using poly(glycidyl methacrylate) (PGMA) as the polymer, a widely available and inexpensive material. We deposit SiN_x by hot wire chemical vapor deposition (HWCVD), a technique in which source gasses are catalytically decomposed at heated filaments, and PGMA by initiated chemical vapor deposition (iCVD), a variant of

HWCVD where an initiator is dissociated into two radicals and starts the polymerization process [5]. In the HWCVD process no highly energetic ions are present and layers can be deposited on any type of delicate substrate.

Using a configuration of two SiN_x layers with a PGMA interlayer we were able to deposit a simple barrier that is pinhole free and has a barrier function sufficient for any sensitive device [6]. Focused ion beam scanning electron microscopy investigations of such structures reveal extremely good adhesion between the organic and inorganic layers, even in degraded (i.e., end of life) samples [7].

In this paper we will examine these multilayers by high resolution transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) and demonstrate that upon deposition of SiN_x on top of iCVD deposited PGMA material, a layer of SiO_xN_y is spontaneously formed. Not only is this an efficient manner of depositing a three layer structure in a two-step process, it additionally provides an elegant deposition method for SiO_x -like materials in a HWCVD process without using possible oxidative source gases. SiO_x or SiO_xN_y layers have been used in other studies in addition to SiN_x layers for their higher plasticity compared to

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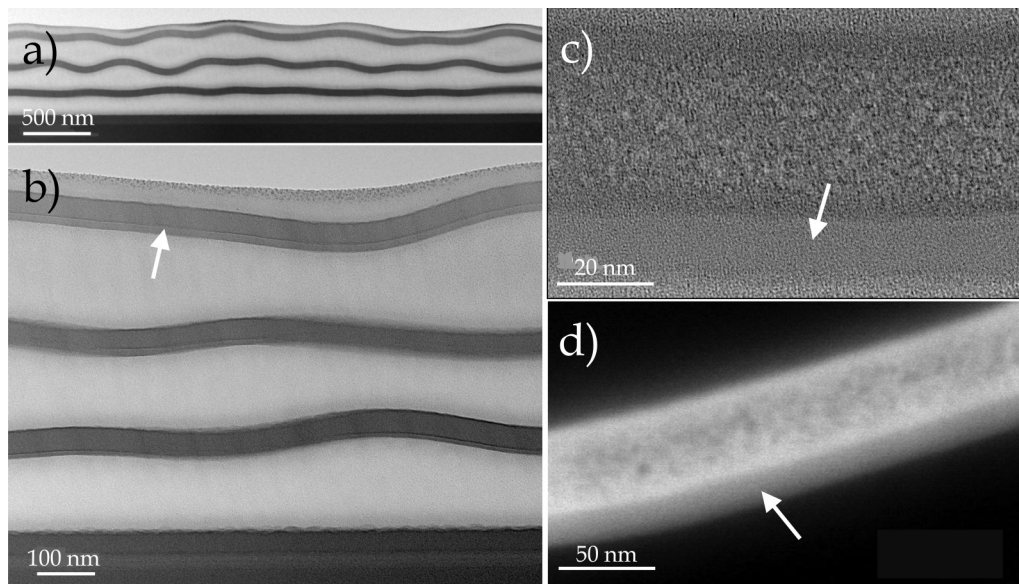
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Fig. 1. Cross-sectional TEM micrographs of our multilayer. (a) An overview and (b) detailed image were made using bright field mode. The dark regions are the SiN_x sublayers. (c) A high resolution image and (d) a high angle annular dark field image of a SiN_x sublayer were made. An additional layer, indicated with arrows, underneath the SiN_x layer is clearly visible in all images.



SiN_x , although the density (and intrinsic barrier function) of SiO_x is lower than that of SiN_x , it can be used to cover defects [8].

2. Methods

Our SiN_x layers were deposited in a multichamber deposition system (PASTA) using pure silane (SiH_4) and ammonia (NH_3) as source gasses. A dedicated low temperature hot wire chamber was used in which the wire–substrate distance can be as large as 20 cm. Radiative heating is reduced drastically in this manner and process temperatures never exceeded 100 °C [9]. The PGMA layers were deposited in a homemade iCVD reactor [10], designed in cooperation with the Massachusetts Institute of Technology labs [11] after their reactor. As a monomer GMA (97%, Aldrich) was used and as an initiator tert-butylperoxide (98%, Aldrich). All samples were deposited on glass.

For high resolution TEM imaging, a Tecnai F20ST/STEM was used at an operating voltage of 200 kV. Bright field mode was used to obtain a high resolution image and high angle annular dark field mode for a high z resolution. Thinning of the samples was done using a Gatan PIPS 691 ion mill.

XPS measurements were performed in a Quantera scanning XPS microprobe from Physical Electronics, using a monochromatic Al $K\alpha$ X-ray source at 1486.6 eV, with an energy resolution of about 0.64 eV at full width at half maximum. The depth profile was made using a 3 kV 3 mm \times 3 mm Ar ion beam for ion milling.

3. Results and discussion

Cross-sectional TEM images of our multilayers are shown in Fig. 1. It can be seen in the images that although the SiN_x is not perfectly homogeneous, the material does not contain any voids or nanocrystals. This was accurately checked by recording images slightly out of focus, which would make voids clearly visible. A more remarkable aspect that can be seen in these micrographs is that underneath every SiN_x layer (between the PGMA and the SiN_x) there is an additional sublayer.

The interface with sublayers underneath each SiN_x layer was examined in energy dispersive X-ray spectroscopy (EDX) mode by scanning a 90 nm line across a SiN_x sublayer. The spectra for all detectable elements are shown in Fig. 2. On both sides of the Si

and N containing region an oxygen-rich region is present. Some oxidation of the top surface of the SiN_x layer (right side of the EDX spectrum) can easily occur as our low temperature SiN_x layers contain around 30% hydrogen and the layers are exposed to air in between depositions.

The amount of oxygen present on the bottom side of the SiN_x , however, is much more significant and the amount of nitrogen is decreased compared to the center part of the SiN_x region. This suggests that upon SiN_x deposition first a SiO_x layer is formed, because of the intermixing of oxygen, which then gradually changes into SiN_x when the oxygen intermixing diminishes as the SiN_x deposition progresses.

Additionally our multilayers were analysed by XPS. Depth profiles, made by recording XPS after successive sputter removal of material for a triple and quadruple layer, are shown in Fig. 3. As sputter rates are unknown for these materials, the elemental composition is plotted against sputter time rather than depth. Because of sputtering, some mixing of materials occurs, which broadens all peaks and decreases the depth resolution of the elemental composition. At the very surface, however, no mixing has occurred and an N/Si ratio of ~ 0.85 is found. This ratio is confirmed by Rutherford backscattering – elastic recoil detection measurements (not shown here). In both profiles shown in Fig. 3, oxygen-rich regions are again found, confirming our EDX measurements. Although different layers are clearly visible, the accuracy decreases with depth, as materials are mixed by the etching. At 0 min no mixing has occurred and the elemental composition is very accurate. A very small O 1s peak is found around 0 min (at the surface of the multilayer), which is probably because of the oxidation of the surface. A thicker O-rich layer is again found at the depth where SiN_x was deposited on PGMA. It can be seen in the XPS spectra that the oxygen content in the bulk PGMA material is lower than expected: this should be around 3/7 considering the GMA monomer ($\text{C}_7\text{H}_{10}\text{O}_3$), which contains, next to one oxygen atom in its backbone, one double-bonded oxygen atom, and one oxygen atom in an epoxide ring (hydrogen atoms are not detected in the XPS measurement). This indicates that the SiO_xN_y sublayers are formed with oxygen released from the PGMA upon exposure to the SiN_x deposition conditions. This may be a result of the

Fig. 2. Spectra of different elements from the EDX experiment, taken over a 90 nm line, crossing a SiN_x - SiO_x layer. It can be seen that on the left side (which is the initially grown material) of the inorganic sublayer, compared to the main SiN_x layers, some of the Si as well as the N atoms are substituted by oxygen.

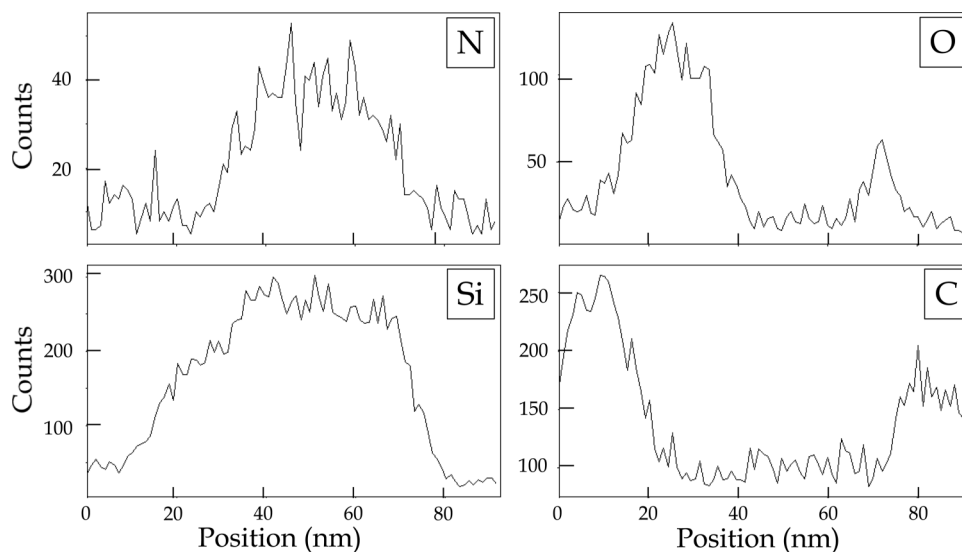
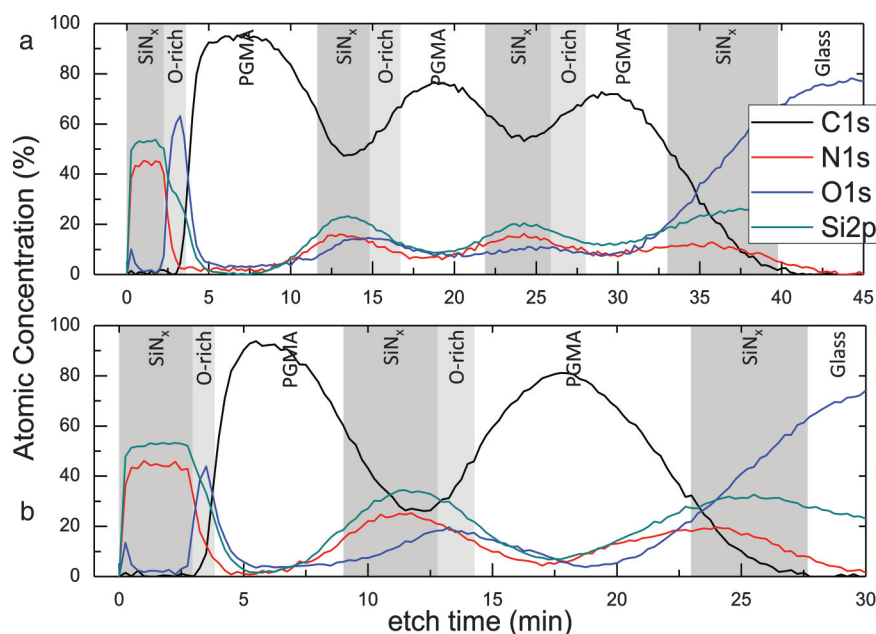


Fig. 3. XPS etching profile of multilayers containing (a) four SiN_x layers and (b) three SiN_x layers. As etching rates for our materials are unknown, the profile is plotted against etching time.



highly reactive atomic hydrogen present in the process. Using the FTIR measurement it was found that the epoxide group as well as the double bonded oxygen is removed from the PGMA [10]. Surprisingly, removal of the latter, supposed to be a more stable group, was found to be faster. On the other hand it may be caused by epoxide ring opening reactions, which are known to occur in the presence of amine species, in this case NH_3 [12,13]. The epoxide ring opening reaction can also result in a chemical bond of the carbon atom from the epoxide ring with NH_2 or SiH_3 groups, which could explain the strong adhesion between the PGMA and inorganic layers.

We believe that the observed interlayers can be beneficial for our barrier's performance and that the reaction involved in their

formation can be an explanation for the extremely strong adhesion between our inorganic and organic layers. Furthermore, this method provides an elegant method for the deposition of an oxide material without using oxidative gasses. A requirement for the success of this method might be the use of iCVD for the deposition of polymers with epoxy groups, which ensures an almost 100% retention of functional groups, in this case the very important epoxide ring and double bonded oxygen group [14].

4. Conclusion

Using high resolution transmission electron microscopy imaging in combination with EDX line profiling, it was revealed that

upon HWCVD deposition of SiN_x on top of PGMA, deposited by iCVD, initially an oxygen rich SiO_xN_y layer is formed. XPS measurements show that this is a result of oxygen atoms being released from the PGMA material, which react with atomic H and (or) amine species. This elegant mechanism, which allows for the deposition of SiO_x material without using oxidative source gasses, can be beneficial for the performance of moisture barriers as SiO_x like materials are used in addition to SiN_x to cover defects. Furthermore, epoxide group ring opening reactions in the PGMA could explain the high interfacial adhesion between the inorganic and organic layers.

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