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科学研究費助成事業　　研究成果報告書

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研究課題名（和文） VUV光ゲルコンバージョン法による高性能薄膜バリア層の開発

研究課題名（英文） Development of High Performance Thin Film Encapsulation by VUV Photochemical Gel Conversion

研究代表者

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研究成果の概要（和文）：室温で窒素雰囲気中に真空紫外線（VUV）を照射することで、ペルヒドロポリシラザン（PHPS）由来のSiNy層を用いて超高性能なガスバリア性薄膜を開発した。VUVの光線量とともにSi-Nネットワークの形成と原子の再配置により、膜内の自由体積が減少し、SiNy層の密度が増加したことが分かった。しかし、VUV照射量と膜厚が増加するにつれて、体積収縮による内部応力により、クラックが拡大しはじめ、最終的にはバリア性能が低下した。膜厚とVUV線量を最適化し、実用レベルの耐久性を実現でき、水蒸気透過率（WVTR）の値は4.8 × 10−5 g m−2 d−1で達成された。

研究成果の学術的意義や社会的意義

これらの研究成果には、国内外の論文や学会で発表され、2020年の薄膜材料デバイス研究会、2021年の第59回高分子と水に関する討論会（高分子学会）、2022年の第83回応用物理学会秋季学術講演会、国際会議IDW（The 29th International Display Workshops）では、奨励賞を受賞する等の高い評価を得た。この研究成果は、印刷で作った薄膜のバリアとしては世界最高性能であり、長期的にはエレクトロニクスデバイスのみならず、食品や医療などの包装分野でも応用が期待される。

研究成果の概要（英文）：This research has successfully developed a low temperature solution-processed high performance gas barrier thin-film using perhydropolysilazane (PHPS)-derived SiNy layers by VUV irradiation under N2. It was found that the density of SiNy layers increased with increasing VUV dose due to the formation of Si-N networks accompanied by removal of H2. The denser and the thicker the film, the higher its barrier performance became. However, cracks widened as the VUV irradiation dose and film thickness increased due to the internal strain caused by the volume shrinkage, eventually resulting in poor barrier performance. By optimizing the conditions with a film thickness of 200 nm and a VUV dose of 12 J/cm2, the best barrier properties in terms of WVTR value of 4.8×10-5 g/m2/day were achieved with a total layer thickness less than 1 um, thus making them suitable for use in flexible organic devices, as well as in other applications.

研究分野：　機能薄膜材料

キーワード：　Photochemical conversion　gas barrier　solution process　VUV irradiation　Polydimethylsiloxane　perhydropolysilazane　metal oxide　thin film encapsulation

１．研究開始当初の背景

Organic light-emitting diodes (OLEDs) are expected to become the next-generation of displays and lighting, due to their ability to be produced in large-areas through a low-cost, roll-to-roll (R2R) manufacturing process using flexible film substrates (FOLEDs). However, OLEDs are vulnerable to moisture and oxygen and require glass encapsulation, which decreases flexibility and adds weight. To protect OLEDs from the environment, a thin film encapsulation (TFE) with alternating stacks of inorganic and organic materials is used. The inorganic material works as a barrier to block water vapor and dioxygen, while the organic material enhances the flexibility. However, such complex structures are currently only achievable through vacuum deposition techniques, like sputtering, chemical vapor deposition (CVD) and molecular/atomic layer deposition (MLD/ALD), involving multiple deposition chambers, which can be time and energy consuming, making these methods expensive and limiting their applicability to small-area devices. To maximize the potential of FOLED technology, developing a solution process for high-performance TFEs is necessary, to reduce costs and manufacture large-area devices.

２．研究の目的

The popular sol-gel method of dense ceramic thin-film deposition requires high-temperature thermal treatment, making it incompatible with both sensitive organic active materials and plastic film substrates. Therefore, we are focused on exploring a non-heating annealing method, using high energy vacuum ultraviolet (VUV) light ($\lambda = 172$ nm) to convert precursors into solid films. By utilizing Polydimethylsiloxane (PDMS) solution precursors, we have successfully formed a PDMS/SiO_x multilayer that can be applied directly to the OLED without any damage. However, the barrier performance of this PDMS/SiO_x film was not enough, so we further explored perhydropolysilazane (PHPS) as a potential barrier material. We are able to coat the PHPS layers on PDMS/SiO_x and then convert it to SiN_y with VUV irradiation, achieving a much higher TFE barrier performance with a water vapor transmission rate (WVTR) of the order of 10^{-3} g/m^2/day.

The main goal of this project is to improve the barrier performance of PHPS layers to meet the requirement of WVTR of 10^{-5} g/m^2/day for FOLEDs. In addition to exploring the potential of photochemical gel conversion, various crystalline and amorphous metal oxide thin films, such as ZnO, SnOx and TiOx, have been synthesized through VUV irradiation of metal-organic precursors. Their functionalities have been found suitable for applications beyond TFEs, such as a color-tunable photoluminescent core-shell thin film and an electron injection layer for an inverted OLED device.

３．研究の方法

Thin film preparation. PHPS was obtained from Shin-Etsu Chemical, Japan as a 20wt% solution in dibutyl ether (DBE), further diluted with anhydrous DBE (99.3%, Sigma-Aldrich) to necessary concentrations before spin-coating to control the thickness of the resulting films. The PHPS layers were irradiated with a vacuum UV (VUV) light generated by a Xe_2 excimer lamp ($\lambda = 172$ nm, photon energy = 7.2 eV = 696 kJ/mol) at a distance of 2 mm from the lamp surface to achieve an average irradiance of 20 mW/cm^2, Hamamatsu Photonics or 85 mW/cm^2, MEIRHA-MS-1-152-H-L2, M.D.COM) for a controlled period. These layers were either prepared on (100) cut Si single crystal wafer or on PI/PDMS samples for characterizations.

Thin film characterization. The film thickness and refractive index (n at 850 nm) were measured on a J.A. Woollam VASE 32 spectroscopic ellipsometer. Fourier transform infrared (FTIR) transmission spectra were measured on a Thermo Fisher, Nicolet is50. The WVTR of the PHPS layers deposited on the PI/PDMS film were measured by the modified differential pressure method on a Super-Detect (effective permeation area: 40 mmΦ, MORESCO) at 40 °C and 90% relative humidity. Cross section of a PDMS/PHPS coating on Si substrate was fabricated on a focused ion beam (FIB) and observed by transmission electron microscope (TEM) measurements using an analytical electron microscope (ARM200F, JEOL Ltd.). X-ray photoelectron spectroscopy (XPS) and Dynamic secondary ion mass spectrometry (D-SIMS) depth profiles were measured by K-Alpha+ (Thermo Fisher Scientific) and ADEPT1010 (Physical Electronics) instruments (Sumika Chemical Analysis Service, Ltd.), respectively.

４．研究成果

4.1 FTIR spectra and refractive index

The PHPS solution was spin-coated onto a Si wafer and its photochemical conversion was studied under VUV irradiation in an N_2-glovebox. Figure 1 shows the changes in the FTIR spectra (a) and the refractive index/film thickness measured by ellipsometry (b) under various VUV irradiation time ranging from 0 to 2500 min for a more detailed analysis of the conversion process. IR absorption peaks representing Si-N vibration of the main chain (830 cm^{-1}) increased, while those representing Si-H vibration (2,163 cm^{-1}) and N-H vibration (3,374 cm^{-1}) decreased in intensity. Furthermore, the refractive index (n@850 nm) increased from 1.55 to 1.73, while the film thickness decreased from 357 to 270 nm following a 2500 min VUV irradiation. These FTIR and ellipsometry observations can be attributed to the formation of Si-N bonds, where the N-H bonds undergo preferential cleavage while some of the Si-H bonds remain, which leads to inter-chain Si-N bonds that solidify the layer.

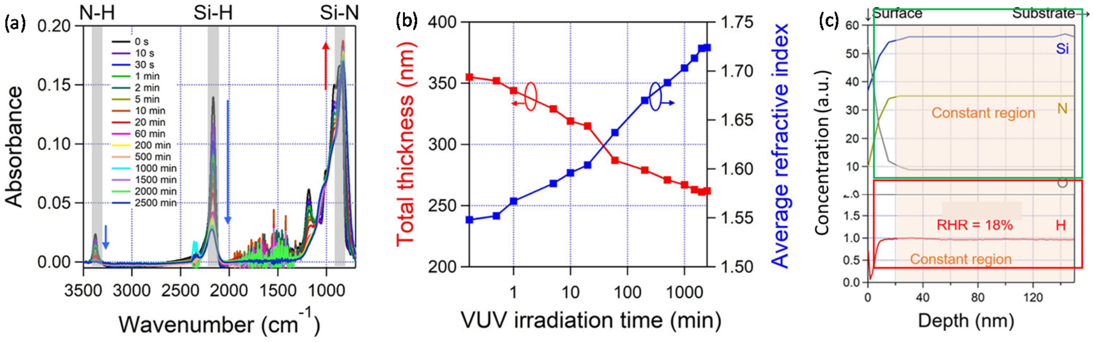

Figure 1. (a) FTIR spectra and (b) film thickness and refractive index of PHPS layers as a function of VUV irradiation time. (c) XPS depth profile of Si, O, N (green, above) and D-SIMS depth profiles of H (red, below) for a PHPS layer irradiated by VUV for 20 min.

4.2 XPS and D-SIMS spectra

XPS and D-SIMS depth profiles of Si, O, N, and H element signals were measured for a PHPS coating irradiated by VUV for 20 min (Figure 1c). The very surface had only a small amount of N, but O accounted for more than 50% instead, the composition was close to SiO_2. As the depth increased, the composition gradually changed into SiN_y, accompanied by a significant reduction in O concentration. H concentration was measured by D-SIMS. The change in H concentration followed the same trend as that of N--zero at the very surface, increasing gradually, and reaching a constant when the surface layer went deeper than 20 nm.

It is evident that the surface of PHPS is converted to SiO_2 when it reacts with residual O_2 even in the N_2-filled glovebox and releases NH_3, while the internal volume is cross-linked by the formation of Si-N bonds accompanied by the removal of H_2 to solidify as SiNH.

4.3 Fabrication of PDMS/PHPS layer for WVTR test

For WVTR measurement, a PI/PDMS film was spin-coated with a PHPS layer. The elastic PDMS was critical in providing the necessary flexibility to the layer, thus avoiding cracks in the PHPS layer. Moreover, to improve the surface wettability and promote better adhesion of the PHPS layer, the PI/PDMS surface was exposed to VUV-treatment, which converted it to a SiO_x surface. As a result, a cross-sectional TEM image of the seamlessly connected PDMS/PHPS layer was presented in Figure 2a, without any cracks or pinholes. The WVTR values of the PI film and the PI/PDMS structure were 9.0 and 1.0 g/m^2/day, respectively. These values are much lower than the WVTR of 10^{-2}~10^{-4} g/m2/day for the PI/PDMS/PHPS layer, indicating that the total barrier performance is not affected by the PI or PDMS layers.

4.4 Effect of VUV intensity

The effects of VUV intensity on the refractive index of PHPS films and their barrier performance were investigated, as shown in Figures 2b and c. The refractive index of the PHPS layers prepared at the same VUV does, but using different lamp powers (20 and 85 mW/cm^2) were found to be almost the same, indicating that the densification of the PHPS layer depends only on the VUV dose, and not the intensity. The WVTR values of the PHPS layers were 1.8×10^{-4} g/m^2/day with a lower intensity, and 2.2×10^{-4} g/m^2/day with a higher intensity. Therefore, the VUV intensity does not significantly influence the densification of the PHPS layer or its barrier performance. However, due to its shorter irradiation time, higher VUV intensities can help to speed up the process.

4.5 Effect of VUV does

The barrier performance is influenced by the film density, which is directly related to the VUV dose. Figure 3a shows the refractive index of PHPS layers (with a thickness of 200 nm) increases with increasing the VUV dose, but the barrier performance was improved when the VUV dose was increased from 6 to 12 J/cm^2 and then decreased with further VUV irradiation. The poor barrier performance with low VUV dose is due to an insufficient density of PHPS layer, whereas too much VUV irradiation causes the formation of cracks, resulting in poor barrier performance.

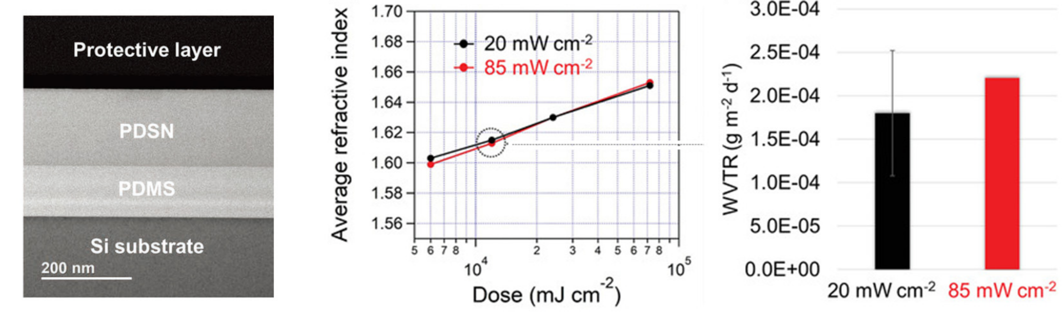

Figure 2. (a) Cross section TEM image of PDMS/PHPS layers on Si substrate. (b) Refractive index of PHPS layers prepared with different VUV intensity (20 or 85 mW/cm^2). (c) WVTR values of PHPS layers prepared with different VUV intensity at a VUV dose of 12 J/cm^2 and a thickness of 200 nm).

4.6 Effect of film thickness

Figure 3b shows the changes in the WVTR values for PHPS layers of various thicknesses prepared at a VUV dose of 12 J/cm². As the layer becomes thicker, up to 250 nm, the barrier performance improves, but then begins to degrade with further increases in thickness. When the layer is thinner than 150 nm, the barrier performance may be poor due to a lack of an effective blocking layer. However, at a thickness of 500 nm, the performance degraded by more than two orders of magnitude compared to that of the 250 nm thick layer. This can be attributed to the increased internal stress in the barrier layers, which caused increased cracking as the film thickness increased.

4.7 The optimized WVTR value

By optimizing the VUV dose and film thickness, the WVTR value of one unit PDMS/PHPS layer on PI film was achieved to be 2.2×10^{-4} $g/m^2/day$ at a temperature of 40˚C and a relative humidity of 90%. This value was further improved to 4.8×10^{-5} $g/m^2/day$ with a alternating stacks (3 units of PDMS/PDSN, as seen in Figure 3c), which is the best performance to date for all solution-processed TFE. Such WVTR value meets the requirements for OLEDs, and a total thickness of the TFE is less than 1 μm, making it flexible.

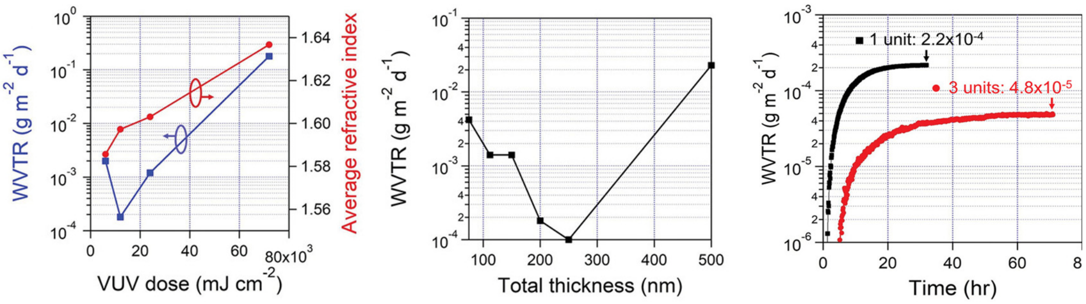

Figure 3. (a) WVTR values and refractive index as a function of VUV dose prepared at a PHPS film thickness of 200 nm. (b) WVTR values as a function of PHPS layer thickness prepared at a VUV dose of 12 J/cm². (c) The optimized WVTR values of one unit and three units of PDMS/PHPS layers coated on PI film substrate.

4.8 Conclusions

This research has successfully developed a low temperature solution-processed high barrier performance TFE using perhydropolysilazane (PHPS)-derived SiN_y layers by VUV irradiation. Barrier performance can be affected by the density, film thickness, and cracks or pinholes. It was found that the density of SiNy layers increased with increasing VUV dose due to the formation of Si-N networks, but it is independent of the VUV intensity. This suggests that increasing the power of the VUV lamp and reducing the irradiation time can help to speed up the process. The denser and the thicker the film, the higher its barrier performance became. However, cracks widened as the VUV irradiation dose and film thickness increased due to the internal strain caused by the volume shrinkage, eventually resulting in poor barrier performance. By optimizing the conditions with a film thickness of 200 nm and a VUV dose of 12 J/cm² , the best barrier properties in terms of WVTR value of 4.8×10^{-5} $g/m^2/day$ were achieved with a total layer thickness less than 1 μm. Such simple and fast solution processing possesses excellent barrier properties against oxygen and water vapor, thus making them suitable for use in flexible organic devices, as well as in other applications.

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掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/admi.202201517	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関