Flexible insulator of hollow SiO_2 spheres and polyimide hybrid for flexible OLED

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ABSTRACT

The fabrication of interlayer dielectrics (ILDs) in flexible organic light-emitting diodes (OLEDs) not only requires flexible materials with a low dielectric constant, but also ones that possess the electrical, thermal, chemical, and mechanical properties required for optimal device performance. Porous polymer-silica hybrid materials were prepared to satisfy these requirements. Hollow SiO_2 spheres were synthesized using Atomic Layer Deposition (ALD) and a thermal calcination process. The hybrid film which consists of hollow SiO_2 spheres and polyimide shows a low dielectric constant of 1.98 and excellent thermal stability up to 500^oC. After the bending test for 50,000 cycles, the porous hybrid film exhibits no degradation in its dielectric constant or leakage current. These results indicate that the hybrid film made of hollow SiO_2 spheres and polyimide (PI) is useful as a flexible insulator with a low dielectric constant and high thermal stability for flexible OLEDs.

INTRODUCTION

There is great interest in OLED displays because of their thinness, light weight, low power, and potential use in flexible displays.[1-5] For flexible OLED displays, an array of organic thin-film transistors

(OTFTs) is fabricated on a flexible substrate prior to OLED deposition. In conventional TFT backplane technologies, a dense silica film has been used as the interlayer dielectric of integrated circuits (IC), because of its unique properties, such as its good compatibility with silicon, high thermal stability, and good electrical properties.[6-8] However, most inorganic materials cannot be used for flexible displays, because of their rigid characteristics. OTFTs need flexible low dielectric constant (low k) materials instead of the traditional dense silica (k≈4) as the interlayer dielectric to minimize the interconnecting resistance/capacity (RC) delay, cross-talking and power dissipation.[9,10] Therefore, it is necessary to find flexible low k materials both to increase the flexible performance and reduce the power consumption.

Some recent reports have suggested the use of various materials such as porous silica-based materials,[11-13] fluorinated amorphous carbon,[14] benzoxazine-based polymers,[15-17] and organometallic compounds[18] as low k interlayer dielectrics. However, some drawbacks still remain in terms of their thermal, mechanical and chemical properties. Polyimide (PI) has been widely used as an interlayer dielectric material, because of its high temperature durability, good mechanical properties, excellent chemical and thermal stability.[19-21] However, PIs with dielectric constants of about 3.1 to 3.5 are inappropriate for interlayer dielectric applications. In an attempt to lower the dielectric constant while maintaining good mechanical, thermal and chemical properties, on this study inorganic hollow spheres were introduced into a PI film.

Herein, we report the synthesis of hollow SiO_2 spheres to form a porous low k material. Polystyrene (PS) beads were used as a sacrificial template and a thin SiO_2 layer was coated onto it using atomic layer deposition (ALD). We made a metal-insulator-metal structure to measure the dielectric constant of the hollow SiO_2 spheres covered with polyimide film. The hollow SiO_2 spheres with PI hybrid film had insulating properties and a low dielectric constant of 1.98, as compared to the original PI dielectric constant of 3.45. The hybrid film showed excellent thermal stability up to 500 ^{o}C and retained its electrical properties after the bending test for 50,000 cycles. The hollow SiO_2 spheres structures did not deform after bending. It is reported that the agglomeration of SiO_2 spheres and dispersion has been observed when the hollow SiO_2 spheres mixed with PI solution coated on substrate [22]. To avoid agglomeration of hollow SiO_2 spheres, we have not mixed the hollow SiO_2 spheres with PI solution. The sequential deposition process is helpful to make film in a simple way by which we can skip the procedure of dispersion of hollow SiO_2 spheres in the PI solution.

RESULTS AND DISCUSSION

Figure 1a shows a schematic of the experimental procedure employed to make the MIM structure consisting of hollow SiO_2 spheres with PI hybrid film to measure its current-voltage (I-V) characteristics, and dielectric constant and subject it to the cyclic bending test. The mono-disperse anionic PS beads were prepared by emulsion polymerization. The PS beads were dispersed in DI water (0.75 wt%) and their outer surfaces were terminated with the –OH group. After O_2 RIE treatment of the substrate, the solution was spin coated on the substrate. After drying at 80 ^{o}C for 20min, the PS beads were completely dried. **Figure 1**b shows the well distributed PS beads on the substrate. The diameter of the PS beads was approximately 230 nm. SiO_2 was deposited on the PS beads by plasma enhanced ALD. An O_2 plasma was used as the oxygen source during the oxidation step in the ALD cycle. The SiO_2 thickness was 10 nm. After calcination at 350 ^{o}C for 1h, the PS beads inside the SiO_2 shell were completely removed. We broke hollow SiO_2 spheres intentionally by razor blade to check whether PS bead in SiO_2 shell removed or not after calcination process. It has been observed that there was no breakage of hollow SiO_2 spheres after removing PS beads and PI solution was not detected inside the hollow SiO_2 spheres. **Figure 1**c shows the hollow SiO_2 spheres. ALD allows for precise thickness control, optimal large-area uniformity, and good step coverage. High quality SiO_2 was reported to be obtained by thermal oxidation of the Si surface at temperatures > 800 ^{o}C. However, the plasma assisted ALD process demonstrated the low temperature synthesis of SiO_2 with high quality in a short time.[24]

The PI (10 wt%) solutions were spin coated on the hollow SiO_2 spheres. **Figure 1**d shows the FE-SEM cross sectional image of the hollow SiO_2 spheres with PI hybrid films. This result shows the good compatibility of the hollow SiO_2 spheres with PI. In general, silica and PI hybrid films made using the sol-gel method with silica contents larger than 10 wt% were reported to be opaque and contain coarse silica particles.[22] In our study, an ALD deposition process was developed for SiO_2 employing $SiH_2(N(C_2H_5)_2)_2$ (Air Liquide SAM.24) and an O_2 plasma. The ALD process with this precursor leads to high quality SiO_2 films over a wide temperature range.[24]

Considering the high temperatures involved in the TFT backplane process after ILD deposition, the dielectric material has to be thermally stable at temperatures higher than 400 ^{o}C. We used thermally stable polyimide which monomer materials of polyamic acid are Tetracarboxylic acid and dianhydride and Diamine. Polyimide was synthesized from polyamic acid after polymerization at 300~350 ^{o}C. Figure 2a shows the structure of PI. We conducted a thermogravimetric analysis (TGA) of the hybrid film at a heating rate of 10^{o}C/min from room temperature to 800 ^{o}C under an air atmosphere. **Figure 2b** presents the TGA curves of the hollow SiO_2 spheres with polyimide hybrid film. The weight of the hybrid films remains almost the same as that of the original film below 400 ^{o}C. The hybrid films show a 6 % weight loss at a temperature of 500 ^{o}C. This result is attributed to the evaporation of the residual NMP solvent. The weight of the hybrid film decreased considerably above 570 ^{o}C, because of the decomposition of PI. These results suggest that the hollow SiO_2 spheres with polyimide hybrid film have the good thermal stability required for flexible OLEDs.

Before measuring electrical properties of hollow SiO_2 spheres with PI hybrid film, we calculated the volume fraction of hollow SiO_2 spheres in hybrid film. The volume fraction of hollow SiO_2 spheres was 0.32. The leakage current of the hollow SiO_2 spheres with PI hybrid film was measured. As shown in **Figure 3**a, the leakage currents of the hybrid film and PI were 2.0×10^{-13} A and 1.6×10^{-12} A at a voltage of 30 V, respectively. **Figures 3**b and **3**c represent the current densities of the hybrid film and PI as a function of the electric field. The current densities of the hybrid film and PI were 1.26×10^{-9} A/cm^2 and 7.23×10^{-7} A/cm^2 at an electrical field of 1 MV/cm, respectively. The leakage current of the hollow SiO_2 spheres with PI hybrid was one order of magnitude lower than that of PI. In general, ALD SiO_2 films exhibit an outstanding surface morphology and low leakage current. The SiO_2 film in the hollow SiO_2 spheres with PI acts as an electron barrier, so its leakage current was smaller than that of the PI films.[25, 26]. We carried out capacitance-voltage (C-V) measurements between -3V and +3V at 1 Mhz and calculated the dielectric constant from the equation $C=\varepsilon_r\varepsilon_0 A/d$, where C is the capacitance, ε_r is the relative static permittivity, ε_0 is the electric constant ($\varepsilon_0\approx 8.854\times10^{-12}$ Fm^{-1}), A is the area of the electrode and d is the separation between the electrodes. **Figure 3**d shows that the hollow SiO_2 spheres hybrid film has dielectric constant of 1.98, while PI has a dielectric constant of 3.45. The hollow SiO_2 spheres with PI hybrid film have a lower k value than PI, due to the porosity resulting from the hollow SiO_2 spheres. The dielectric constant is decreased from 3.45 to 1.98 by using common commercial PI. The dielectric constant of 1.98 is very good compared to that of previously reported PI based films.[27]

A flexible ILD used for flexible OLEDs should exhibit stability in its electrical and mechanical properties after the bending test. **Figures 4**a **and 4**b shows the leakage current and dielectric constant as a function of the number of bending cycles up to 50,000 cycles (bending radius: 3 mm). In general, porous materials including silica have weak mechanical properties.[28] When porous silicates are bent, the porous structures are exposed to stress, which causes them to deform and eventually fail. The hollow SiO_2 spheres with PI hybrid film retained their I-V characteristics and dielectric constant after 50,000 cycles of bending, as shown in **Figure 4.** The mechanical properties of the PI films were excellent and exhibited a very high tensile strength and modulus [29]. The good mechanical and electrical stability of the hollow SiO_2 spheres with PI hybrid film are due to the compatibility of the hollow SiO_2 spheres and PI, as well as the high quality of the SiO_2 layer. As a result, the hollow SiO_2 spheres with PI hybrid can be applied to produce flexible OLEDs with outstanding mechanical and electrical durability during cycling.

CONCLUSIONS

We successfully synthesized hollow SiO_2 spheres using PS beads as a template and atomic layer deposition (ALD). The hollow SiO_2 spheres consist of 230 nm hollow cores and 10 nm SiO_2 shell. The hybrid film consisting of SiO_2 hollow spheres and PI shows a lower dielectric constant of 1.98, as compared to 3.45 for PI. The hybrid film was thermally stable up to 500°C and retained its electrical properties after the bending test for 50,000 cycles with a leakage current lower than 1.5×10^{-11} A at a voltage of 30 V.

EXPERIMENTAL SECTION

Synthesis of hollow SiO_2 spheres: PS beads (bead content: 0.75 wt%, particle size: ~ 230 nm, solvent: DI water) were spin-coated on an Au coated polyimide substrate at 2000 rpm. After drying for 30 min at 80°C, 10 nm SiO_2 was deposited on PS beads using Plasma Enhanced Atomic Layer Deposition (PEALD; SYNOS Display korea) at 80 °C. To remove the PS beads in the SiO_2 spheres, the SiO_2 coated polystyrene beads were put in a furnace and annealed at 350 °C for 1 h in air ambient. The average diameter of PS beads was 229.58nm from Figure 1(b). The thickness of SiO_2 shell was 10nm from ellipsometry measurement. PS beads were removed by annealing at 350 °C for 1h in air ambient from Figure 1(c). We ensured the hollow SiO_2 sphere consisting of 229.58nm hollow cores and 10nm SiO_2 shell were formed. In this way, hollow SiO_2 spheres consisting of ~230 nm hollow cores and 10 nm SiO_2 shell were formed.

Film processing and characterization: After synthesizing the hollow SiO_2 spheres, poly(amic acid) solution (10wt% of NMP) was spin-coated onto them at 3500 rpm. The PAA film was then cured on a hot plate in N_2 ambient. The temperature was increased slowly to 200 °C and kept at this temperature for

1 h and then increased to 300 °C and kept at this temperature for 1 h to form a PI film. The thickness of the hollow SiO_2 spheres with PI hybrid film is about 430 nm. To measure the dielectric constant and current-voltage characteristic, we prepared a metal-insulator-metal (MIM) structure by depositing the hollow SiO_2 spheres with PI hybrid film on metal electrodes (Ti:10 nm/Au:65 nm) coated on a 125 μm thick PI substrate. Top electrodes (Ti: 10 nm/Au: 65 nm) were deposited on the hollow SiO_2 spheres with PI hybrid film using a shadow mask with holes 200 μm in diameter using electron beam evaporation.

Characterizations: The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM, Oxford INCA system, JSM6700F). The thermal stability of the sample was examined by thermogravimetric analysis (TGA, SEICO, TG/DTA6100). The current-voltage (I-V) and capacitance-voltage (C-V) characteristics were measured by a probe system, viz. a Keithley 4200-SCS electrometer (Keithley Instruments inc.). The bending characteristics were measured by motor controllable motion controller. The testing conditions of bending test were 3mm bending radius and 2 μm step resolution in air ambient.

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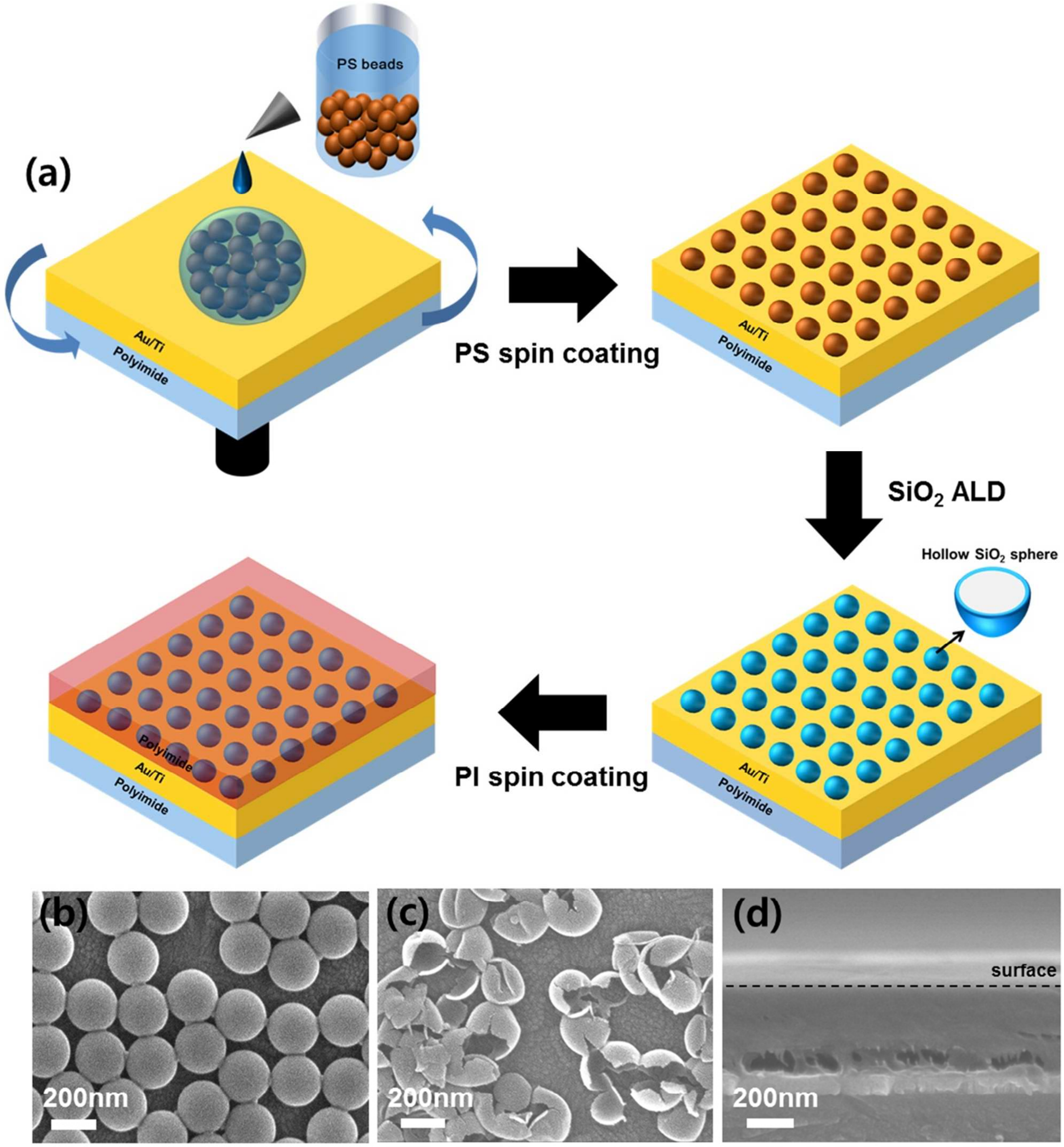

Figure 1. (a) Schematic of the synthesis of the composite film which consists of the hollow SiO_2 spheres and PI. **(b)** SEM image of SiO_2-coated polystyrene beads on Au/Ti coated PI substrate. **(c)** SEM image of hollow SiO_2 spheres. **(d)** cross-sectional SEM image of hybrid film consisting of hollow SiO_2 spheres with PI.

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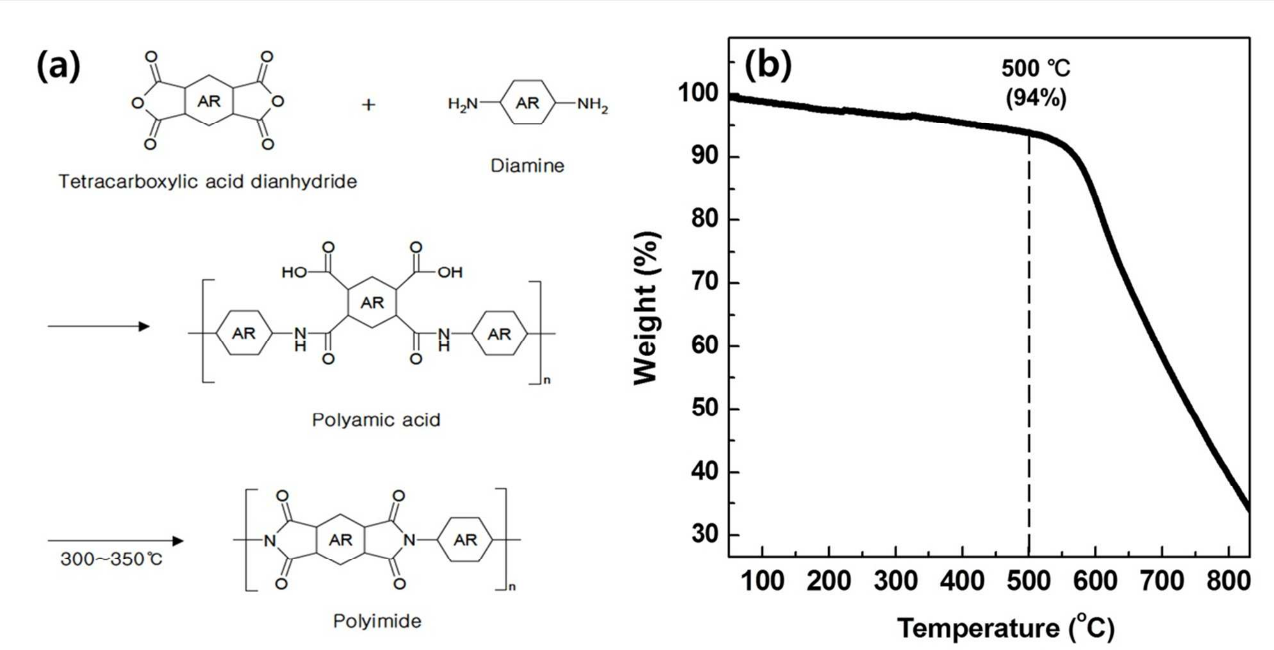

Figure 2. (a) The structure of PI. **(b)** TGA curves of the hollow SiO_2 spheres with PI hybrid film.

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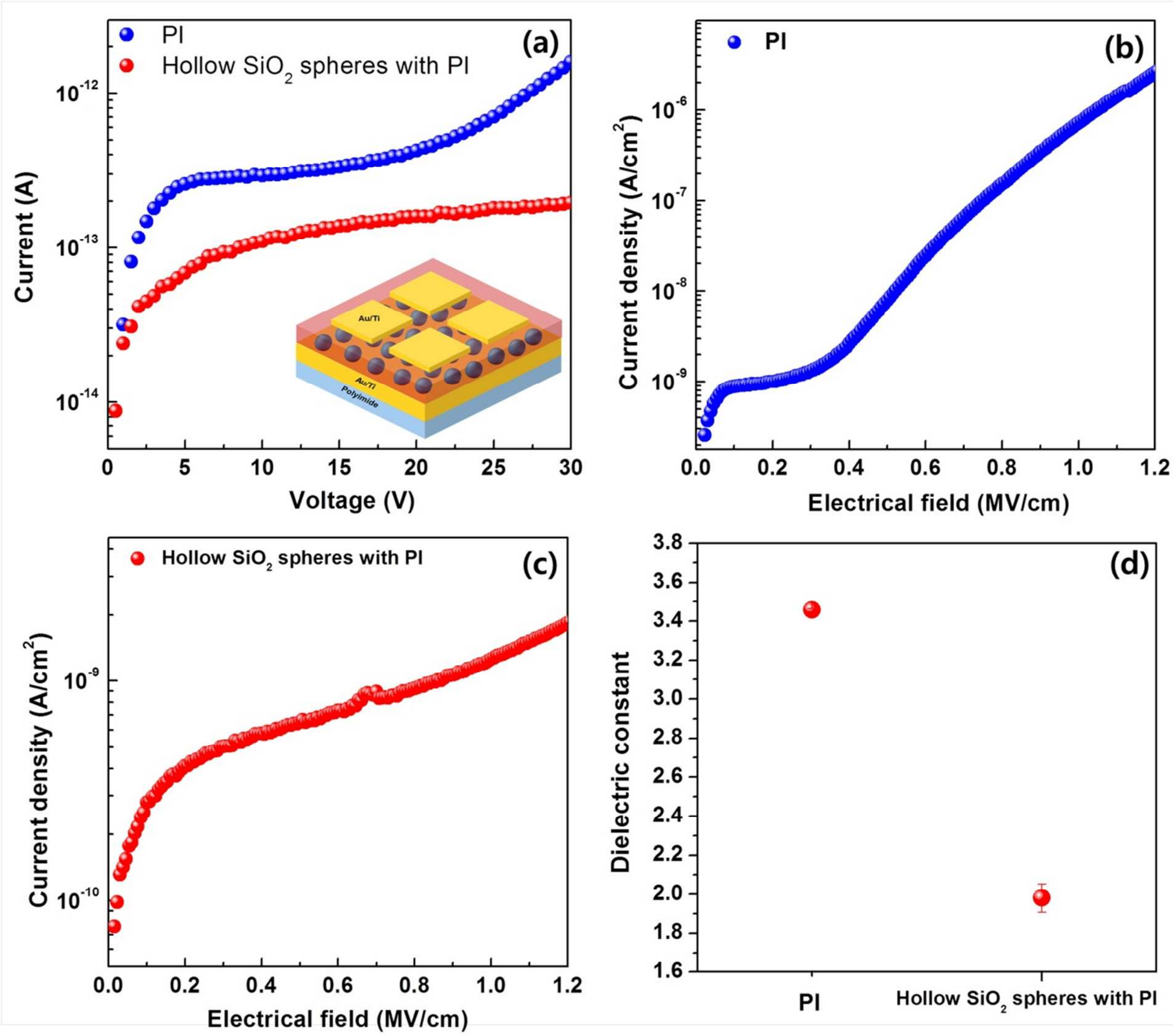

Figure 3. (a) Current-voltage characteristics of PI film and those of the hybrid film. **(b)** Variation of current density with electrical field of PI film. **(c)** Variation of current density with electrical field of hollow SiO_2 spheres with PI hybrid film. **(d)** Dielectric constant of PI and hollow SiO_2 spheres with PI hybrid film.

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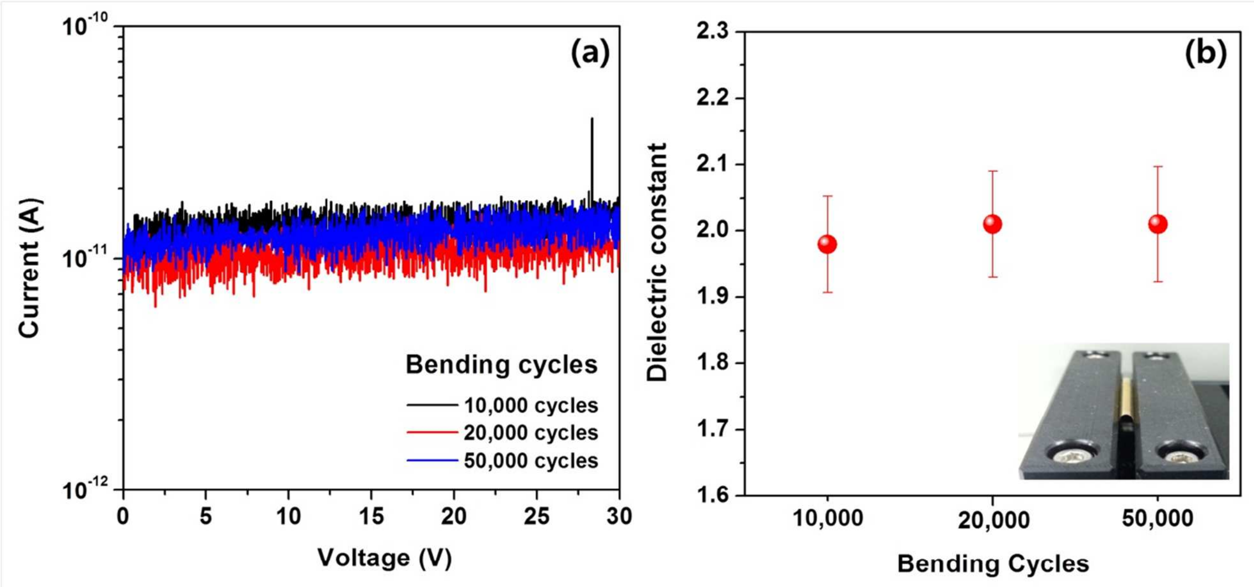

Figure 4. (a) I-V characteristics of hollow SiO_2 spheres with PI hybrid film as a function of number of bending cycles. **(b)** Variation of dielectric constant of hollow SiO_2 spheres with PI hybrid film as a function of number of bending cycles.