Research of Aging Test on High Tg Colorless Polyimide

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Abstract

The colorless polyimide (CPI) has been drawn much attention for its application in transparent electronics, such as the camera under panel (CUP) in organic light-emitting diode display (OLED) display which required a high transmittance (Tr%). The high temperature (even to 450) process of the preparation of OLED device may have huge challenges on the properties of CPI, so we designed a series of aging test experiments to study the influence of test temperature and atmosphere on the Tr% of CPI films with structure of Glass/SiO2/CPI/SiO2. With the increasing of aging temperate from 430 to 450 and 470, the Tr% of the film decrease obvious, especially responding the wavelength from 400nm to 600nm. The samples with aging test all had a low Tr% than the sample without aging. Comparing with the sample without aging, the loss transmission were 0.22%, 1.42% and 4.82% for the films aging with 430, 450 and 470 in N2 atmosphere, respectively. Meanwhile, the influence of aging atmosphere on the Tr% was also researched with nitrogen and air. The film aging with nitrogen had a higher Tr% than that aging with air, the loss transmission were 1.22% and 1.42% compared with the sample without aging test.

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Abstract

For the past few years, the colorless polyimide (CPI) has been drawn much attention for its application in transparent electronics, such as the camera under panel (CUP) in organic light-emitting diode display (OLED) display which required a high transmittance (Tr%). The high temperature (even to 450) process of the preparation of OLED device may have huge challenges on the properties of CPI, so we designed a series of aging test experiments to study the influence of test temperature and atmosphere on the Tr% of CPI films with structure of Glass/SiO_2/CPI/SiO_2. With the increasing of aging temperate from 430 to 450 and 470, the Tr% of the film decrease obvious, especially responding the wavelength from 400nm to 600nm. The samples with aging test all had a low Tr% than the sample without aging. Comparing with the sample without aging, the loss transmission were 0.22%, 1.42% and 4.82% for the films aging with 430, 450 and 470 in N_2 atmosphere, respectively. Meanwhile, the influence of aging atmosphere on the Tr% was also researched with nitrogen and air. The film aging with nitrogen had a higher Tr% than that aging with air, and the loss transmission were 1.22% and 1.42% compared with the sample without aging test. The properly process temperature and inert atmosphere were selectively methods to keep a high Tr% of CPI films for preparing transparent electronics device.

Author Keywords

Colorless polyimide, transparent electronics, aging test, aging atmosphere, loss transmission

Introduction

As known, polyimide (PI) have extensive applications in the aerospace industry, microelectronic and optoelectronic engineering, organic light-emitting diode display (OLED), and separation membrane due to their high-temperature resistance, outstanding mechanical properties, chemical and radiation resistance, and excellent dielectric properties.[1-4] PI is also introduced into the OLED device to prepare the flexible substrate for its bendable function. For the past few years, the colorless polyimide (CPI) has been drawn much attention for its application in transparent electronics, such as the camera under panel (CUP) in the OLED display which require a high transmittance (Tr%).[5-7] However, the high temperature (even to 450) process of the preparation of OLED device may have huge challenges on the properties of CPI, so we designed a series of aging test experiments to study the influence of high temperature and atmosphere on the Tr% of CPI films with structure of Glass/SiO_2/CPI/SiO_2, as showed in Figure 1a. The sample 10, sample 12 and sample 14 were aging with 430, 450 and 470 for 120 min in N_2 atmosphere, respectively.[8-11]The sample 8 was without any aging test and sample 11 was aging with 450 for 120 min in N_2atmosphere. Both the five samples (sample 8, sample 10, sample 11, sample 12 and sample 14) were all with a structure of Glass/SiO_2/CPI/SiO_2.[12-14]

As showed in Figure 1b, the transmittance of samples based on different structures and aging test were also measured to research the influence of high temperature on the yellow index (YI) of CPI. With the increasing of aging temperate from 430 to 450 and 470, the Tr% of the film decrease obvious, especially responding the wavelength from 400nm to 600nm., the films with aging all had a low Tr% than which without aging. For the samples with structure of Glass/SiO_2/CPI/SiO_2, the loss transmission were 0.22%, 1.22% and 4.82% for the samples (sample 10, sample 12 and sample 14) aging with 430, 450 and 470, in N_2 atmosphere comparing with the sample without aging (sample 8). The author thought that the higher temperature may damage the polymer distribution in the CPI film, and leading the transparency of CPI films lower. Meanwhile, the influence of aging atmosphere on the Tr% was also researched with nitrogen and air. The film aging with nitrogen had a higher Tr% than that aging with air, which is caused by the oxidation reaction of CPI films during the aging test. The loss transmission were 1.22% and 1.42% for the films aging with nitrogen and air atmosphere. The properly temperature and inert atmosphere were selectively methods to keep a high Tr% of CPI films for preparing transparent electronics device.

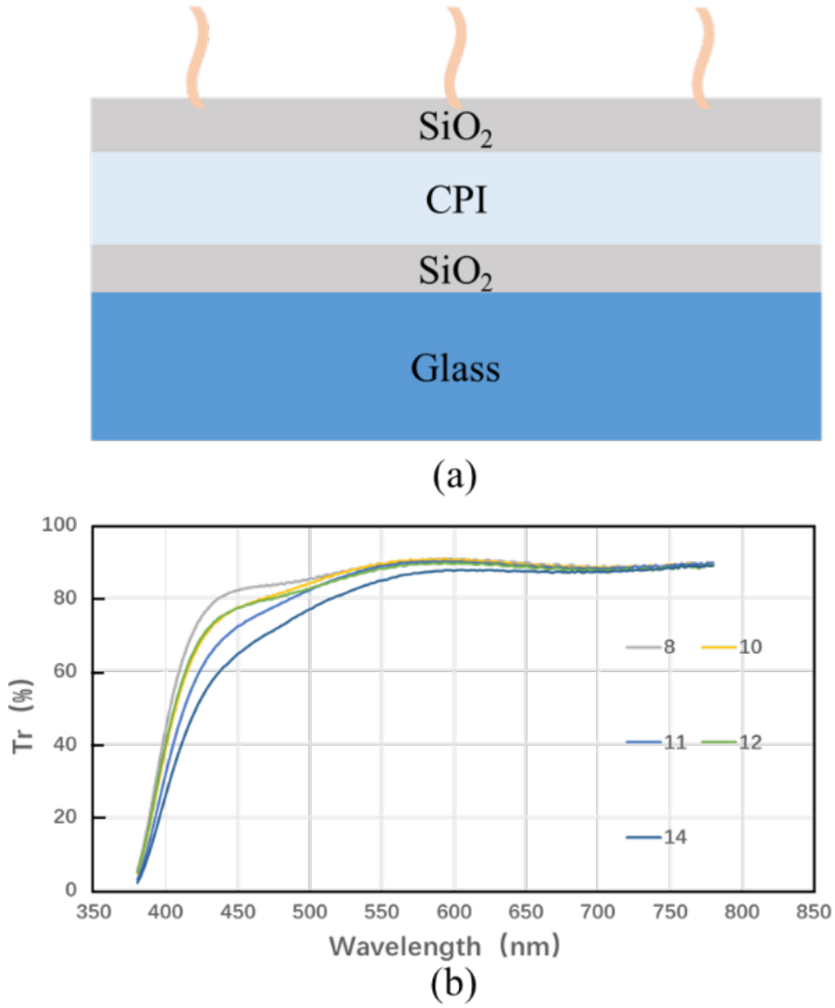

Figure 1. (a) The architecture of the samples for aging test, (b) the transmittance spectra of samples with different aging test

Experimental section

A series of glass substrate with size of 100mm x100mm was cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl, then blown by nitrogen, and dried in an oven at 80 °C overnight. After a deposition of SiO_2 layer with thickness of 600nm formed by plasma enhanced chemical vaper deposition (PECVD) machine, the CPI layer with thickness of 12um was prepared on the SiO_2 layer by spin-coating with a polyamide acid slurry and annealed at 450 °C for 30 min with N_2atmosphere. Then another SiO_2 layer with thickness of 500nm was formed on the CPI layer by PECVD machine. Finally, the samples with size of 100mm x100mm were divided into 50mm x 50mm, and those new samples were placed in air or N_2 atmosphere at 430 °C, 450 °C and 470 °C for 120 min for the aging test, respectively. The data of Tr%, SEM and surface roughness were obtained by spectrophotometer, and atomic force microscope for all the aged samples. In this work, the samples 1 and 8 represented the samples with structure of Glass/SiO_2/CPI and Glass/SiO_2/CPI/SiO_2 without doing aging test, respectively. Samples 2, 4, 6 and 3, 5, 7 represented samples with structure of Glass/SiO_2/CPI with doing aging test at 430, 450 and 470 for 120 min in Air and N_2atmosphere, respectively. While, samples 9, 11, 13 and 10, 12, 14 represented samples with structure of Glass/SiO_2/CPI/SiO_2 with doing aging test at 430, 450 and 470 for 120 min in Air and N_2atmosphere , respectively.

Result and discussion

As presented in Figure 2, the atomic force microscopy (AFM) images were measured to confirm the surface morphology of those aging samples. For the four samples (sample 1, ample 3, sample 5 and sample 7) with structure of Glass/SiO_2/CPI, the sample 1 (sample without aging) had a uniformity CPI film with a surface roughness of 2.51nm distributed on Glass/SiO_2 substrate. While the another three samples with aging at 430, 450 and 470 in N_2 atmosphere for 120 min (sample 3, sample 5 and sample 7) obtained the surface roughness of 6.48nm, 2.72nm and 5.08nm, respectively. The author thought that with aging at high temperature for 120 min and cooling to room temperature, the CPI film on the SiO_2 had a heat expansion and cold contraction process, which may cause the surface of CPI film became rougher. While, it was still unclear that the sample 5 had a similar surface roughness with sample 1. For another five samples (sample 8, ample 10, sample 11, sample 12 and sample 14) with structure of Glass/SiO_2/CPI/SiO_2, the sample 8 (sample without aging) also had a uniformity SiO_2 layer film distributed on Glass/SiO_2/CPI substrate with a surface roughness of 5.11nm. The surface roughness of three samples with aging at 430, 450 and 470 in N_2 atmosphere for 120 min (sample 10, sample 12 and sample 14) were 4.33nm, 6.74nm and 4.98nm, respectively. The sample 11 (with aging at 450 in air atmosphere for 120 min) obtained a surface roughness of 3.28nm.

For the aging samples, we also measured the Focused Ion Beam (FIB) results to confirm the multi-layer structure of samples if damaged during the process of aging test with temperature of 450. Figure 3 showed the FIB results of sample 1, sample 5, sample 8 and sample 12. For the samples with structure of Glass/SiO_2/CPI, the sample 1 had a CPI layer with thickness of 12.78um and the two layers (SiO_2 and CPI layers) all had complete structure without any broken. The sample 5, which was aging in N_2atmosphere with temperature of 450 for 120 min, also had complete structure. Based on the structure of Glass/SiO_2/CPI/SiO_2, the sample 8 without aging had a CPI layer with thickness of 13.47um and the sample 12 aging in N_2 atmosphere with temperature of 450 for 120 min had CPI layer with thickness of 12.78um. The SiO_2 layer on CPI layer was also complete without broken both in the sample 8 and sample 12. The FIB results showed that the CPI layer on will not been damaged.

Based on the structure of Glass/SiO_2/CPI and Glass/SiO_2/CPI/SiO_2, the transmittance of samples measured by a spectrophotometer after aging with different temperature and in different aging atmosphere were showed in Table 1, and the transmittance spectra of few samples were and showed in Figure 4, the Tr% spectra was measured between the wavelength from 380nm to 780nm. As showed in the Table 1, for the samples with structure of Glass/SiO_2/CPI, all the aging samples (sample 2 to 7) had lower Tr%@380˜780nm, 450nm and 400nm than the sample without aging (sample 1). The aging with high temperature may damage the CPI film and cause to increase the YI of CPI film, leading the decrease of Tr% for all the aging samples. For the samples with structure of Glass/SiO_2/CPI/ SiO_2, the aging samples (sample 9 to 12) had close Tr%@380˜780nm, 450nm and 400nm to the sample without aging (sample 8), and the samples aging at 470 (sample 13 and 14) had lower Tr%@380˜780nm, 450nm and 400nm than the sample without aging (sample 8). By introducing an SiO_2 layer on the CPI film, the new adding layer can not only protect the CPI film from being damaged worse during the aging test with a high temperature, but also had an increased transmission effect for the sample. However, the YI of the samples also increased during the aging test, which may cause the drop of Tr%. For the sample 9 to 12, the increased transmission effect of SiO_2 layer and the Tr% drop caused by increased YI may be equivalent, so the four aging samples had close Tr%@380˜780nm, 450nm and 400nm to the sample without aging (sample 8). When the aging temperature increase to 470, the molecular structure of CPI film suffer worse damage than the samples aging with a low temperature, thus leading a greater drop of Tr%@380˜780nm, 450nm and 400nm, especially the sample aging in air atmosphere (sample 13).

As showed in Figure 4a, compared with no aging samples (sample 1and sample 8), the aging samples with structure of Glass/SiO_2/CPI and Glass/SiO_2/CPI/SiO_2 (sample 5 and sample 12) all had an obvious loss of Tr% after aging at 450 in N_2 atmosphere for 120 min. The author thought that the molecular structure of

CPI film was damaged by the high temperature, which lead the YI of the films all increased, and the higher YI had a close connection with Tr%. It was interesting that the sample 8 had a higher Tr% than sample 1, which was caused by the increased transmission effect of SiO_2 on the CPI film. The samples with structure of Glass/SiO_2/CPI/SiO_2were aging at 430, 450 and 470 in N_2 atmosphere for 120 min, respectively. As showed in Figure 4b, compared with no aging sample (sample 8), the all aging samples (sample 10, sample 12 and sample 14) also had lower Tr%. It was worth noting that the sample 10 and 12 had similar Tr% spectra, while sample 14 had an obvious lower Tr% than other 3 samples. The lower Tr% of sample 14 indicated that the aging temperature of 470 had a greater damaged on the molecular structure of CPI film. Finally, the samples with structure of Glass/SiO_2/CPI/SiO_2 were aging at 450 in N_2 and air atmosphere for 120 min, respectively, and the transmittance spectra of three samples (sample 8, sample 11 and sample 12) were showed in Figure 4c. The two aging samples (sample 11 and sample 12) all had lower Tr% than the sample without aging (sample 8). Besides, the Tr% of sample 11 was also lower than sample 12. The different value between sample 11 and sample 12 showed that the aging atmosphere also had an obvious effect on the Tr% of CPI films. When aging in inert gas (N_2), the film may suffer less damage during the whole aging process than aging in active gas (air, oxygen content higher than N_2). The loss values of Tr% after aging for all samples were showed in Figure 4d. It was obvious that the samples without SiO_2 covered on CPI had higher loss of Tr% than corresponding samples with SiO_2 covered on CPI. This interesting phenomenon may be caused by two reasons. The first reason was that the SiO_2 covered on the CPI film had an increased transmission effect for sample, which may restrain the loss of Tr%. The second reason was that the molecular structure of CPI suffer worse damage during the aging test without the protection of upper SiO_2 layer. Researching for the aging test of the sample 1~14, it was clearly that there was at least three effective methods to prevent the Tr% of CPI film to drop serious, which including introducing an inorganic layer with protective effective (such as SiO_2 layer), aging in an atmosphere with inert gas (such as N_2) and aging with a suitable temperature (better no higher than 450).

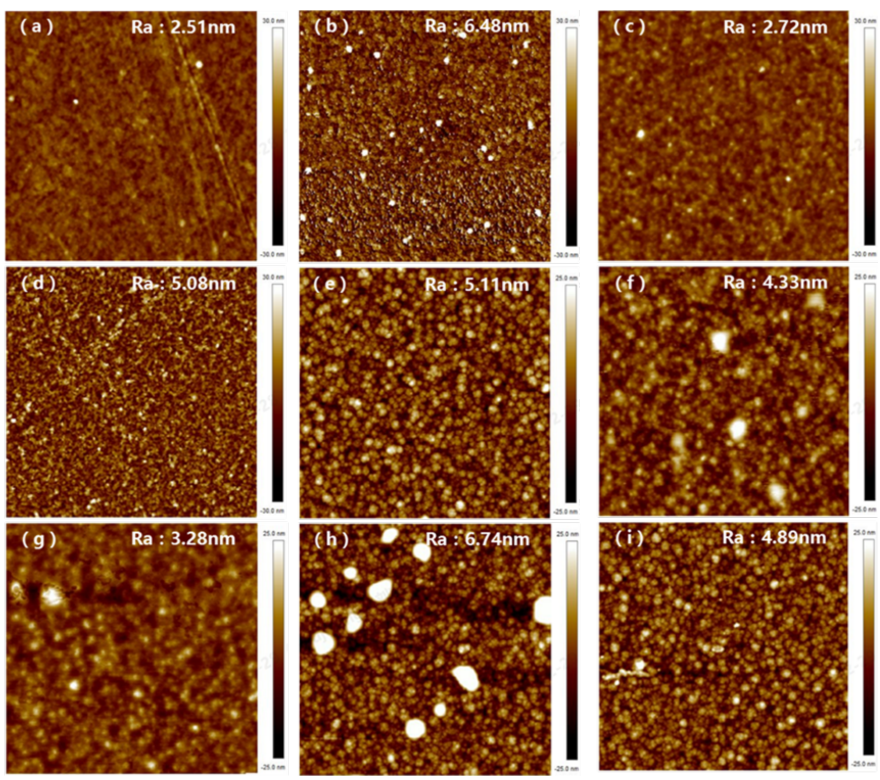

Figure 2. Surface topography (5 μm × 5 μm) of samples: (a) sample 1, (b) sample 3, (c) sample 5, (d)

sample 7, (e) sample 8, (f) sample 10, (g) sample 11, (h) sample 12, (i) sample 14.

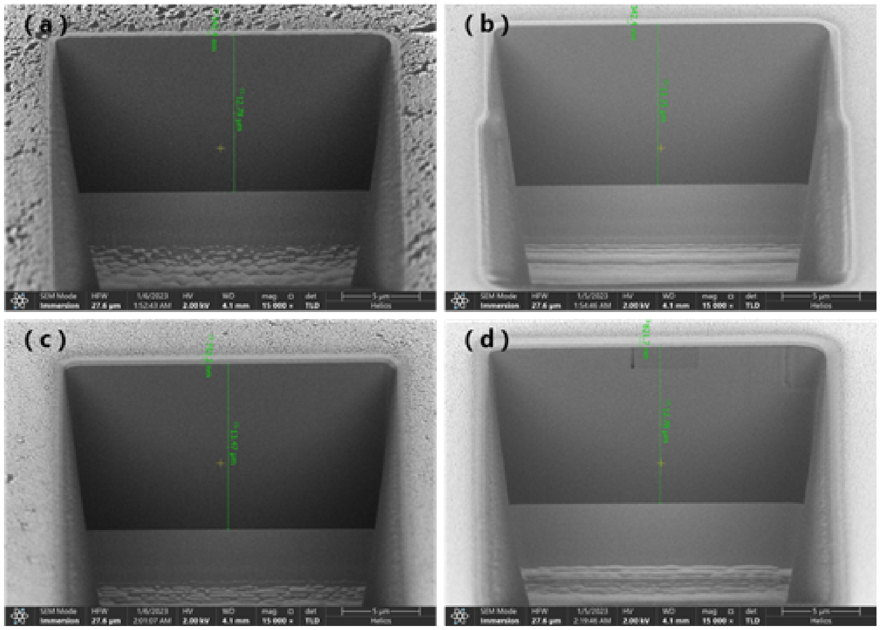

Figure 3. The Focused Ion Beam (FIB) results of samples: (a) sample 1, (b) sample 5, (c) sample 8, (d) sample 12.

Table 1. The transmittance of samples with structure of Glass/SiO_2/CPI and Glass/SiO_2/CPI/SiO_2 after aging with different temperature and in different aging atmosphere.

No.	Structure	Temperature ()	Atmosphere	Time (min)	Tr%@ 380~780nm	Tr%@ 450nm	Tr%@ 400nm
1	Glass/SiO_2/CPI	/	/	/	86.70	80.86	44.89
2	Glass/SiO_2/CPI	130	Air	120	78.23	49.24	16.18
3	Glass/SiO_2/CPI	130	N2	120	75.29	41.07	9.79
4	Glass/SiO_2/CPI	150	Air	120	83.37	59.49	17.88
5	Glass/SiO_2/CPI	150	N2	120	84.71	75.31	38.19
6	Glass/SiO_2/CPI	170	Air	120	79.92	47.18	9.27
7	Glass/SiO_2/CPI	170	N2	120	56.51	14.56	2.05
8	Glass/SiO_2/CPI/SiO_2	/	/	/	88.54	81.99	44.65
9	Glass/SiO_2/CPI/SiO_2	130	Air	120	88.20	76.91	37.82
10	Glass/SiO_2/CPI/SiO_2	130	N2	120	88.32	77.24	39.26
11	Glass/SiO_2/CPI/SiO_2	150	Air	120	87.12	72.13	32.35
12	Glass/SiO_2/CPI/SiO_2	150	N2	120	87.32	77.23	40.40
13	Glass/SiO_2/CPI/SiO_2	170	Air	120	82.93	56.58	17.67
14	Glass/SiO_2/CPI/SiO_2	170	N2	120	83.72	64.67	26.39

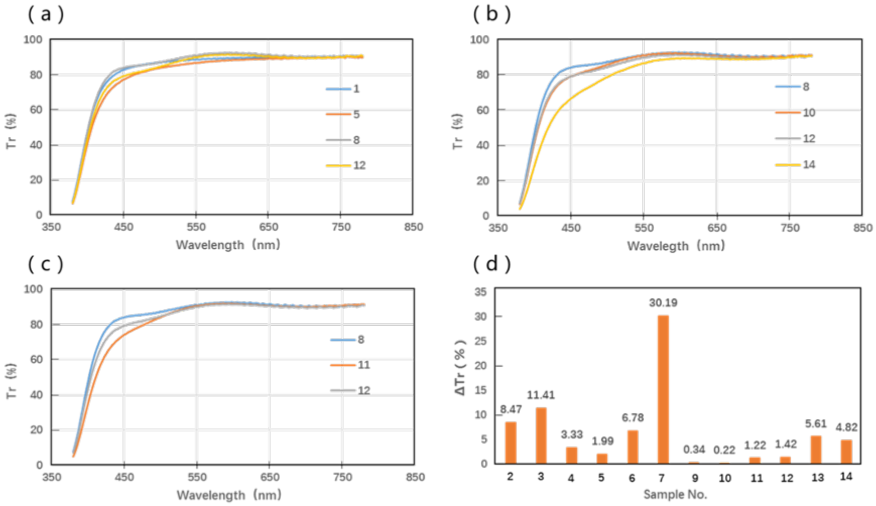

Figure 4. Transmittance spectra of samples with aging test: (a) samples aging with different structure, (b) samples aging with different temperature, (c) samples aging in different atmosphere, (d) the transmittance loss of samples with aging test.

Conclusions

In summary, a series of samples with structure of Glass/SiO_2/CPI and Glass/SiO_2/CPI/SiO_2 were prepared and had aging test with different temperatures (430, 450 and 470) and different aging atmosphere (air and N_2) to study the influence of high temperature on the Tr% of CPI film. It was found that the structure, aging atmosphere and aging temperature all had obvious influence on the Tr% of samples. For the samples with structure of Glass/SiO_2/CPI/SiO_2, with the increasing of aging temperate from 430 to 450 and 470, the Tr% of the film decrease obvious, especially the sample aging with 470 had a drop of Tr%, and all the samples with aging all had a low Tr% than sample without aging. Comparing with the films without aging, the loss Tr% were 0.22%, 1.42% and 4.82% for the films aging with 430, 450 and 470, respectively. The sample aging in air atmosphere also got a lower Tr% than the one aging in N_2 atmosphere. When aging with 450 in N_2 atmosphere for 2h, the sample with structure of Glass/SiO_2/CPI/SiO_2 had a higher Tr% than sample with structure of Glass/SiO_2/CPI/SiO_2, which was caused by the increased transmission effect of SiO_2 on the CPI film. The sample with structure of Glass/SiO_2/CPI had similar principle with Glass/SiO_2/CPI/SiO_2. To increase the quality of transparent electronics device, it is worth to introduce the CPI in the application of the preparation of device and there are at least of three strategies to guarantee the Tr% of CPI. The relative lower process temperature (which can meet the demand the request of), the inertia protection gas and increased transmission effect layer can all guarantee the Tr% of CPI film during the preparation process of transparent electronics device.

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Notes

The authors declare no competing financial interest.

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