of an irreversible path in the film [1]. In contrast with the difference in the first oxidation potentials, the as-deposited and the annealed MgPc behaved in similar manners for the subsequent redox cycling, i.e., they showed reduction and oxidation potentials of −0.40 and +0.60 V (versus SCE), respectively (see Fig. 2 and [1]).

The as-deposited MgPc film has an intense absorption maximum at around 685 nm with a shoulder at around 650 nm. After the oxidation, the bluish film changed to purple, since the 685 nm peak decreased and the 550 nm peak grew. After the first oxidation reduction cycling, the absorption spectrum recovered to that of the virgin film (Fig. 3, curve a1). Similar spectral features of the as-deposited MgPc have been reported elsewhere [1].

The absorption spectrum of the annealed film (Fig. 3, curve b1) is red shifted and broadened compared with that of the virgin MgPc. The absorption of the metal phthalocyanine has been recognized to shift toward a longer-wavelength region by heat treatment [6]. A slight change in the absorption spectrum or a colour change in the heat-treated film is seen after the first oxidation. In contrast, after the first oxidation reduction cycling (Fig. 3, curve b2), the film showed a similar absorption spectrum to that of the as-deposited MgPc (Fig. 3, curve a1).

Fig. 4 shows FTIR absorption spectra for the as-deposited and the annealed samples, together with the results after the first oxidation and the first oxidation-reduction. Typical absorption lines cited in the text are listed in Table 1, where the numbering system of Sidorov and Koltun [3] is adopted. Absorption line 8 of the virgin film (774 cm⁻¹), characteristic of the α-phase, disappears and a new absorption line 9 (780 cm⁻¹) appears after heat treatment. This resulted from the α → β transition of MgPc [3, 10]. Doubles are seen for lines 20 and 28 of the annealed film. The appearance of these doubles are also peculiar to β-MgPc [10, 11]. Absorption line 20 and line 28 become a single line after the first oxidation, indicating that the oxidation of β-MgPc induces a structural transition other than β. Absorption line 8 of annealed MgPc (780 cm⁻¹) is unaltered after the first oxidation and shifts to 774 cm⁻¹ of the α polymorph after the first oxidation reduction. The result is consistent with that of the visible absorption mentioned already. Absorption line 18 (1078 cm⁻¹) of the as-deposited film is attributed to C–N stretching vibration of the
MgPc molecule [10] and is related to the colour change of the film. Absorption line 18 of the virgin film shifts toward a lower-energy region after the first oxidation and recovers to that of the as-deposited after the first oxidation reduction. As for the annealed film, absorption line 18 scarcely changed for redox cycling, which also agrees with the result of the visible absorption of this film. In summary the following results are obtained:

1. The potential barriers for anions to migrate through MgPc films at the first oxidation is higher in β-phase films than in α-phase films.

2. Stretching of carbon nitrogen bonds in the phthalocyanine rings causes the electrochromism, or the reversible colour change, of MgPc. Oxidation of as-deposited (α-phase) films leads to a change in colour from blue to purple while that of the heat-treated (β-phase) films does not lead to any colour change.

3. Oxidation of β-phase films induces structural transformation to a phase other than β.

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References

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