課題番号　：F-21-HK-0058
利用形態　：機器利用
利用課題名（日本語）　：プラズモン誘起 2 光子フォトクロミック反応の定量測定
Program Title (English)　：Quantitative measurements of plasmon-induced two-photon photochromic reactions
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キーワード／Keyword　：リソグラフィ・露光・描画装置、成膜・膜堆積、分析、フォトニクス

1. 概要（Summary）

Nanoparticles of noble metal such as gold show intense color which is derived from localized surface plasmon resonances (LSPRs). LSPRs which are collective oscillations of conduction electrons give rise to the enhancement of electromagnetic field in the vicinity of nanoparticles. Therefore, various optical effects such as surface-enhanced Raman scattering and plasmon-enhanced photochemical reactions are induced. In this study, locally-induced plasmon-enhanced two-photon photochromic reactions have been studied.

2. 実験（Experimental）

【利用した主な装置】

・超高精度電子ビーム描画装置 100kV
・電界放射型走査電子顕微鏡
・原子層堆積装置

【実験方法】

Au nanogap dimer with a gap width of 5 nm have been fabricated by electron beam lithography and lift-off techniques on the glass substrate. Polyvinyl acetate film including merocyanine (MC) with appropriate concentration was spin-coated on the substrate with a thickness of ~100 nm. A femtosecond laser beam (λ_p: 800 nm, τ: 100 fs, f: 80 MHz) was irradiated on the substrate to promote the photochromic reaction of MC to spiropyran. Absorption and extinction microspectroscopy were employed to monitor the reactions.

3. 結果と考察（Results and Discussion）

It was found from the change in absorbance values that it was a primary reaction, and it was confirmed that the reaction was via a two-photon absorption process of MC from the experiments with various laser powers. Comparing the reaction rate constants between bulk and Au nanogap dimer showed a slight increase in reaction rates in Au nanostructures, but no significant difference. This is because the polymer film has a thickness of ~100 nm, whereas the reaction proceeds only near the surface of the Au nanogap dimer. We propose a method for analyzing the reaction with high sensitivity based on the change in the refractive index value due to the reaction as shown in Fig. 1(a). LSPR band shows a dramatic blue-shift because the refractive index value of the reaction site changes due to the locally-induced photochromic reaction. Fig. 1(b) shows the irradiation time dependence of ln [MC] in the film without Au nanostructures and that on Au nanostructures. The reaction rate of MC on Au nanogap dimer accelerated about 20 times than bulk by utilizing LSPR band shift for reaction analysis. This reaction is almost complete in 60 s.

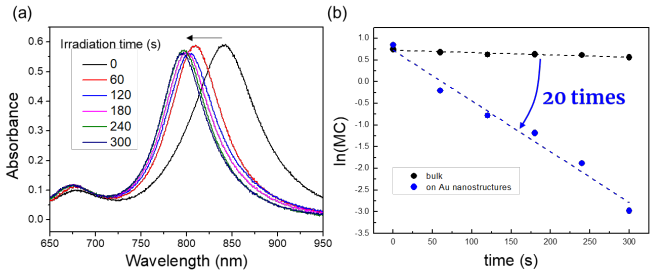

Fig. 1 (a) LSPR bands with various irradiation time. (b) The irradiation time dependence of ln [MC] in the film without Au nanostructures and that on Au nanostructures.

4. その他・特記事項（Others）

共同研究者：上野貢生（北大院理）

5. 論文・学会発表（Publication/Presentation）

なし

6. 関連特許（Patent）

なし