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論文の内容の要旨

In this thesis, analytical approach of local surface contribution (electric dipole) and nonlocal bulk contribution (magnetic dipole and electric quadrupole) of chromium metal was presented by examining the nonlinear optical response of V-shaped nanohole arrays. The optical second harmonic generation data achieved in this work would give rise to the intriguing phenomenon of metamaterial. Additionally, controlling the optical behavior of Cr nanostructures will make a significant impact for optical device application.

In the field of plasmonics, gold or silver was widely adopted as the substrate material because they are favorable for surface plasmon resonance (SPR) where the electromagnetic waves could be confined to propagate along the interface between two media [1,2]. Since these metals have very poor adhesion, chromium is usually employed as a reliable adhesion layer before depositing Au or Ag thin film and shaping the structures. Nevertheless, according to my calculation, plasmon excitation of Cr is possible and more feasible compared with part of the other metals. Indeed, A. Shalabney et al. found surface plasmon resonance in Cr columnar thin film in the Kretschmann configuration [3]. In addition, to avoid SPR's loss, a very thin and uniform film is required and Cr is the best material [4]. Because of its importance in plasmonics it is very necessary to address the optical behavior of Cr. Within this aim, the goal of my work is considering the optical response of Cr metal in nanoscale.

Objectives

There are various approaches used to reveal the optical properties of metallic nanostructure. Among these, surface second harmonic generation (SHG) method has become a potential technique, which is very sensitive to the structures lacking inversion symmetry. Thus, V-shaped Cr nanoholes should generate strong SHG intensity. The nonlinear optical response should be recognized in the obtained second order nonlinear susceptibility tensor elements. From second order optical standpoint, plasmonics has been expected to improve the nonlinear efficiency as well as shrink the nonlinear components in size. Noticeably, the recent reports researched on the second order optical effects in plasmonic structures have emphasized that metal materials give rise to a very complicated state, especially at nanoscale [5,6]. Both surface (electric dipole) and bulk (magnetic dipole and electric quadrupole) contributions can appear equally in the SHG magnitude whereas the surface term is usually considered as feasible candidate. Up to now, examination of dipole and multipoles terms in the geometric nanostructrues is still the significant challenge of second order optical effects. Thus, clarifying the role of the local surface and nonlocal bulk contribution becomes particularly necessary to control and optimize the nonlinear optical behavior of the metallic nanostructures for the functional applications. Furthermore, as far as I know there is no information available on surface second harmonic generation of Cr metal. Hence, in my work, the attention was paid on the proper estimation between dipole and multipole effects in V-shaped Cr nanohole structure. The new information could contribute to well understanding of nonlinear optical effects occurring in artificial materials.

Experimental Result

In this research, I have fabricated the arrays of V-shaped nanoholes (see Fig. 1) by JEOL JBX-9300FS Electron Beam Lithography System and measured the azimuthal angle dependence of the SHG intensity. The phenomenological analysis indicated that four nonlinear susceptibility elements including $\chi^{(2)}_{313}$, $\chi^{(2)}_{322}$, $\chi^{(2)}_{311}$, and $\chi^{(2)}_{333}$ present the predominant contribution as shown in Fig. 2. Here 1-axis presents the bisector of the V shape passing through its apex in the sample surface plane. 2-axis is perpendicular to 1-axis and lies on the sample surface, too. 3-axis is normal to the sample surface plane (see Fig. 1(b)).

As for the origins of $\chi^{(2)}_{311}$, $\chi^{(2)}_{322}$, and $\chi^{(2)}_{333}$ elements, it is impossible to distinguish between the contribution of the V-shaped Cr nanoholes and the bare Cr substrate since these two susceptibility elements appear simultaneously under C_s (V-shaped hole) and C_∞ (bare Cr substrate) symmetries.

On the other hand, the contribution of the nonlinear susceptibility element $\chi^{(2)}_{313}$ should be purely from the nanoholes because it emerges owing to the

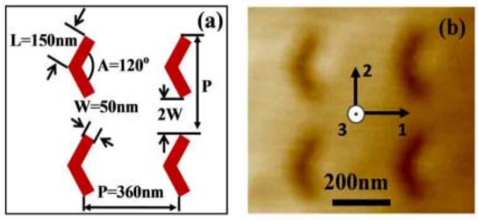

Fig. 1. Structure of V-shaped subwavelength nanohole array: (a) scheme of the designed parameters, (b) atomic force microscopy image.

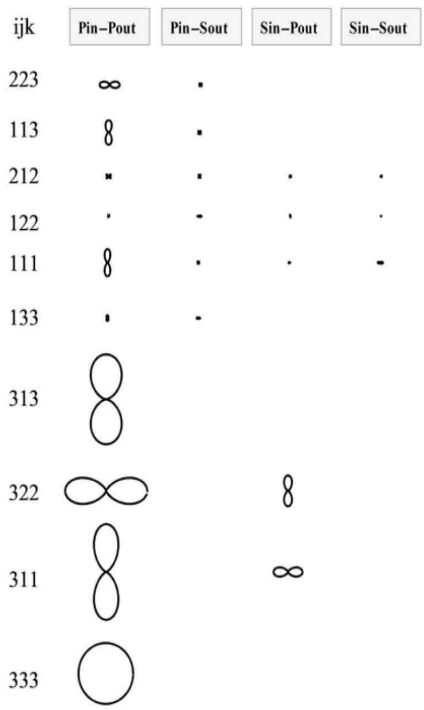

Fig. 2. Decomposition of SHG intensity from V-shaped nanoholes when one of the nonlinear susceptibility elements $\chi^{(2)}_{ijk}$ is set equal to a calculated value and all the other elements are set equal to zero. The intensities are arbitrary but on a common scale. ijk are the suffices of the nonlinear susceptibility elements.

symmetry breaking in 1-axis created by the V-shaped nanoholes. For favorable material exploited for artificial nanostructures such as gold, plasmon exciation enhancing nonlinear optical effect could be accomplished. However, in the case of Cr metal plasmon was silent when I examined the physical origin of the large contribution of the $\chi^{(2)}_{313}$ element. Interestingly, the observed SHG response was attributed to the nonlocal bulk contribution of the Cr metal. Under scrutiny, there are vertical metallic sidewalls within each V-shaped hole leading to existence of air-chromium metal boundaries. This has a strong effect on the field gradient in 1-axis because of the rate of spatial change of the field at the boundary of the nanohole surface. The field gradient were thus found to induce considerable contribution of $\chi^{(2)}_{313}$. In particular, instead of local surface contribution (electric dipole effect), nonlocal bulk contribution (higher multipole effects) demonstrated predominance with respect to the SHG signal. It is fascinating insight of the V-shaped Cr nanohole arrays since local surface contribution is usually the feasible candidate. My achievement implies the fact that the nonlinear optical behavior of the metamaterials should not be merely treated by usual electric dipole approximation because it is not sufficient to provide the comprehensive description. In metal nanostructures, there is an inherent complication since the reflected SHG signal generally contains both surface and volume nonlinear contributions. The difficulty in estimating the electric dipole and the precise role of higher multipole effects is the issue lasting for long time from the early stages of nonlinear optics and still under intriguing process of examination. Therefore, the proper estimation between surface and bulk effects in my work is particularly essential to improve the understanding of the nonlinear optical response of metal nanostructures and metamaterials.

In a further work, I have attempted to examine the dependence of the SHG response on the structural parameters of V-shaped chromium nanoholes. It is expected to understand the origin of the SHG in problem if we consider how the SHG intensity alters when the arm length and the apex angle are changed. Thus, three sets of the V-shaped nanoholes were fabricated (see Fig. 3) and their SHG intensities in the azimuthal angle dependence were compared with each other. In particular, SHG intensity created by individual V shape increased when the arm length or the apex angle increased (see Fig. 4). A simple model calculation was presented to deduce the experimental results. It provided valuable insight that there was a systematic dependence of the SHG intensity on the designed parameters of Cr nanoholes. The clarification shows that the nonlinear optical behavior resulted from the bulk contribution of metallic electrons. This work therefore provides the new information in adjustment of the nonlinear optical behavior of metamaterial for functional applications.

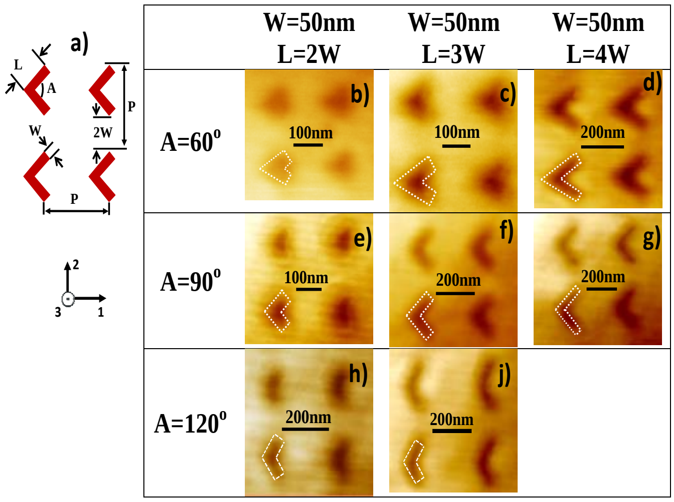

Fig. 3. Structure of V-shaped subwavelength nanohole array: (a) scheme of the designed parameters and atomic force microscopy image of the first set (b-d) of V-shaped arrays with 60° apex angle, the second set (e-g) of V-shaped arrays with 90° apex angle, and the third set (h-j) of V-shaped arrays with 120° apex angle. The dotted line shows the designed "V"-shapes.

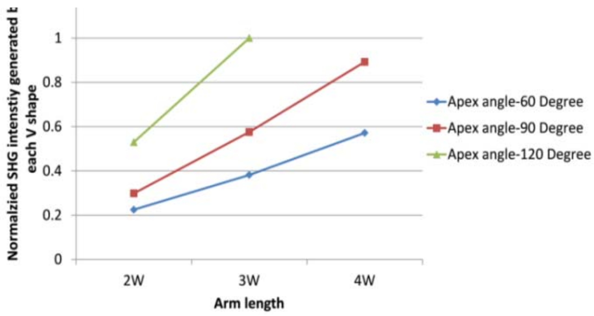

Fig. 4. The normalized SHG intensity emitted from each V shape.

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LIST OF PUBLICATION

1. Ngo Khoa Quang, Yoshihiro Miyauchi, Goro Mizutani, Martin D. Charlton, Ruiqi Chen, Stuart Boden, and Harvey Rutt, "Optical second harmonic generation from V-shaped chromium nanohole arrays", Jpn. J. Appl. Phys. **53**, 02BC11-1- 02BC11-5 (2014).
2. Ngo Khoa Quang, Yoshihiro Miyauchi, Goro Mizutani, Martin D. Charlton, Ruiqi Chen, Stuart Boden, and Harvey Rutt, "Optical second harmonic generation of V-shaped

chromium nanoholes---dependence on the structure parameters of the nanoholes", Surf. Interface Anal. (2014).

Keywords: Second harmonic generation (SHG); Cr metal; Nanoholes; V-shaped structure; bulk contribution.

論文審査の結果の要旨

本論文では、発展の著しい光通信におけるルーチング技術などに応用可能な非線形光学物質の開発として、非対称な V の字の形を持つナノホール列をクロム薄膜上に微細加工し、その二次の非線形光学効果を、光第二高調波発生（SHG）現象を観測することにより検出した。そして、その応答の加工パラメータ依存性および、非線形光学効果の物理的起源についての知見を得ることができた。

ナノホール列の設計と作製は英国サウサンプトン大学と共同で行った。石英ガラス基板上に厚さ 15 ナノメートルの Cr 膜を蒸着し、電子ビームリソグラフィー法によりナノホール列の作製を行った。V 字型のナノホールの溝の幅 W は５０ｎｍ、腕の長さ L は２W、３W、４W、V 字の頂角 A は A= 60 度、90 度、120 度のものを作った。ナノホール間のピッチは 200ｎｍから 400ｎｍの間の値を選んだ。１つの種類のナノホールのグループは 10μm ×10μm の大きさを持ち、V 字型ナノホールの深さは制御しなかったが、原子間力顕微鏡(AFM)による測定でおよそ５ｎｍとわかった。試料はガラス基板の上に複数作られるが、肉眼ではその位置は見えないので、AFM 測定により位置や形成の完成度を確かめた。

ナノホール列からの SHG の測定の光源はピコ秒の時間幅を持つ Nd:YAG レーザーの倍波出力(波長 532nm)で、試料の反射光に混じって発生する 266nm の光を観測した。肉眼では試料の位置が判別できないので、スライドステージを含む特殊仕様の試料ホルダーを組み立て、直径 1mmφに集光したビームスポットが、常に試料加工部を照射し、なおかつ試料をその法線軸周りに回転させて、反射光の方向が変わらないように慎重に配置のセッティングを行った。

まず L=３W、A＝30 度、ピッチ＝360nm の試料について、SHG の試料回転角依存性を観測した。その結果二次の非線形光学感受率として$\chi^{(2)}{}_{313}$が有意な値を持つことがわかった。ここで添え字の１と３はそれぞれ、各 V 形の中心軸方向、および試料基板の法線方向の座標を表しており、非線形感受率に座標 1 が１個入っていることは、ナノホールの対称性の破れによる二次の非線形感受率が発現したことを示している。この光学的非線形効果の起源を特定するために、非線形感受率の各成分の大きさの比率を解析したところ、他の研究グループにより報告されている Cr 中のプラズモンの効果は認められず、バルクの四重極子以上の高次の分極の空間変化が起源であることがわかった。

なおまた、SHG 強度の構造パラメータ L と A による依存性についても実験データを得て、V 形ナノホールを３つの矩形穴に近似したモデルで説明を試みた。モデルは SHG 強度のパラメーターの依存性をよく説明したが、一部説明できない面もあり、その原因について検討がなされた。

以上、本論文におけるこれらの成果は、新規の人工非線形光学材料の作製法の提案とその非線形光学的な基礎物性の知見として、学術的にもまた光通信技術などへの将来の応用にも貢献するところが大きい。よって博士(マテリアルサイエンス)の学位論文として十分価値あるものと認めた。