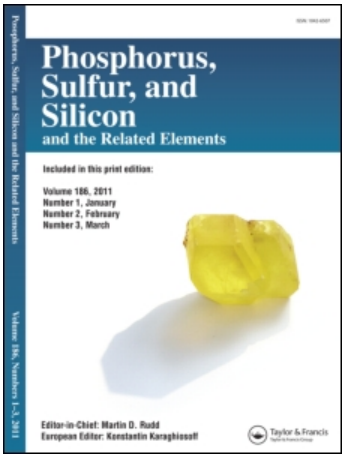


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Metal-Bisphosphonate Multilayer Thin Films with Nonlinear Optical Activity

Grace Ann Neff; Marcus R. Helfrich; Catherine J. Page

To cite this Article Neff, Grace Ann , Helfrich, Marcus R. and Page, Catherine J.(1999) 'Metal-Bisphosphonate Multilayer Thin Films with Nonlinear Optical Activity', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 53 — 56
To link to this Article: DOI: 10.1080/10426509908546180
URL: http://dx.doi.org/10.1080/10426509908546180

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 53-56
Reprints available directly from the publisher
Photocopying permitted by license only

Metal-Bisphosphonate Multilayer Thin Films with Nonlinear Optical Activity

GRACE ANN NEFF, MARCUS R. HELFRICH and CATHERINE J. PAGE

Department of Chemistry and the Materials Science Institute, University of Oregon, Eugene, OR 97403

Multilayer thin films based on metal-bisphosphonate chemistry which possess nonlinear optical (NLO) activity are discussed. Films are prepared in a step-wise fashion using a chromophore-containing asymmetric α,ω-bisphosphonate molecule. Second harmonic generation from these films is reported as a function of number of layers on glass and silicon substrates.

Keywords: nonlinear optical; metal bisphosphonate; thin film; self-assembly

INTRODUCTION

Molecule-based thin film materials with large second-order nonlinear optical (NLO) properties are of great interest currently, due to their potential application in electrooptic, photorefractive, and second harmonic generation devices.[1,2] To incorporate such properties into molecular materials, a polarizable charge situated in an anharmonic potential is required, such as a molecule containing conjugated π systems situated between electron donor and electron acceptor groups. Second-order NLO processes are forbidden in centrosymmetric media under the dipole approximation, and so these molecules must be oriented within the film such that the bulk structure is noncentrosymmetric. Several clever approaches have been examined to align molecules in this manner, including incorporation into poled-polymer and Langmuir-Blodgett films.[3] An alternative technique that has also been shown by several groups to be effective at producing such thin film materials is molecular self-assembly.[1,4-8]

Li *et al.* were the first to make use of the technique of molecular self-assembly to produce acentric films with second-order NLO properties, with their study of siloxane-based multilayers with a high degree of structural regularity and a resulting large NLO response.[2,4,5,9] Katz *et al.* have made use of the technique with a zirconium phosphate/phosphonate system to produce films of acentric multilayers with high second-order optical nonlinearity.[1,10] Recently, Hanken *et al.* have reported the use of similar chemistry to produce noncentrosymmetric multilayers with electro-optical properties.[6]

Our approach to incorporating NLO properties into noncentrosymmetric multilayers involves the layer-by-layer growth of acentric metal-bisphosphonate films,[7,8, 11,12] and is

unique in that it involves only phosphonate linkages, which are less susceptible to hydrolytic cleavage than are phosphates. With this approach, the chromophore-containing bisphosphonate molecule has one of its terminal phosphonate groups protected so that it can bind to a metal-functionalized surface in only one orientation. Following deposition of the molecule, acid hydrolysis is used to convert the ester groups to phosphonic acid moieties in order to enable multilayer growth, as shown in Figure 1. This report describes results using this approach with the chromophore bis(1-ethyl)3-(N-methyl-((4-((4-phenyl-phosphonic acid)azo)phenyl)amino)decyl)phosphonate, or azobenzene molecule I.

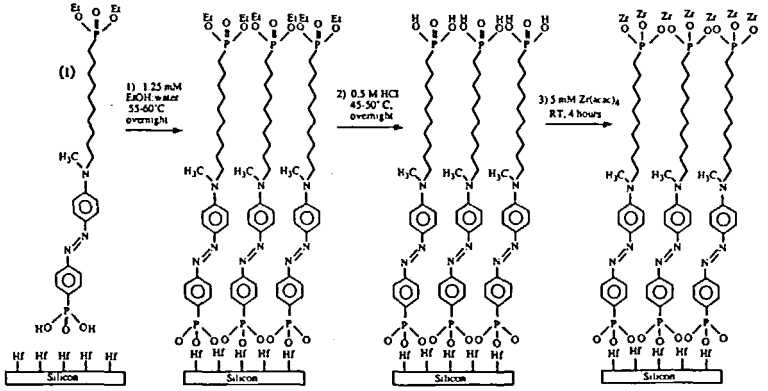


FIGURE 1. Layer-by-layer growth of thin film multilayers of oriented metal bis(phosphonates), illustrated here with use of azobenzene molecule I and Zr.

Multilayers of I and Zr were grown on silicon and glass substrates and characterized with ellipsometry, UV-Vis spectroscopy and second harmonic generation (SHG). The chromophore within molecule I should have quite a large molecular second-order hyperpolarizability.[3] Multilayers of Zr and I on both Si and glass substrates were examined by SHG as a function of number of layers. The results are reported herein.

EXPERIMENTAL

Details of the synthesis of I and the multilayer deposition are reported elsewhere.[8] Substrate preparation and ellipsometry measurements were done as described in reference [13]. Second harmonic generation (SHG) measurements were performed using the 800 nm output of a regeneratively amplified Ti:Sapphire laser operating at 1 kHz.[8]

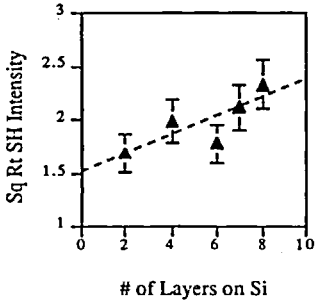
RESULTS

The Si samples studied were prepared on the same Hf-primed substrate, with successive pieces cut from the larger whole after deposition of a certain number of layers. Five

samples, with 2, 4, 6, 7 and 8 layers respectively, were individually characterized with ellipsometry and SHG. The former technique qualitatively verified regular film growth, while the latter enabled us to characterize the NLO properties of the films.[8] The macroscopic second-order NLO response of the bulk film, represented by $\chi^{(2)}$ in the expression below, is dependent on both the orientational average of the microscopic molcular (β) and the number of molecules or layers present in the film (N).

$$\chi^{(2)} \propto N \langle\beta\rangle$$

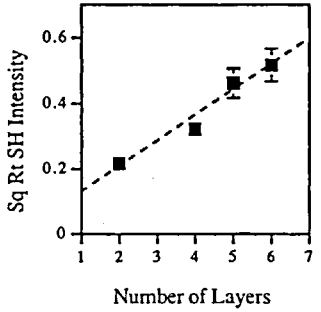
Accordingly, we expect the SH response to increase (quadratically) with increasing number of layers deposited. The square root of the SH response from multilayer samples on Si is plotted in Figure 2, and shows the expected response.



$y = 0.085x + 1.519$
$r^2 = 0.635$

Figure 2. Square root of the SH response as function of number of layers of azobenzene molecule I and Zr on Hf-primed Si substrate

Four different pieces of glass slides served as substrates for four multilayer samples that were grown simultaneously, and each was characterized individually with both UV-Vis Spectroscopy and SHG. UV-Vis spectroscopy was used to verify that roughly the same amount of chromophore was deposited in each azobenzene deposition step. The absorbance increased linearly with each successive layer deposited. The SH response from these multilayers also confirms regular film growth, as shown in Figure 3.



$y = 0.077x + 0.049$
$r^2 = 0.962$

Figure 3. Square root of the SH response as function of number of layers of azobenzene molecule I and Zr on Hf-primed glass

The expected linear increase in square root of the SH response with each subsequent layer is observed for these multilayers also. The data in Figures 2 and 3 indicate that films of roughly the same quality with similar properties can be prepared on either Si or glass substrates, and illustrates that our method of layer-by-layer assembly of metal bis(phosphonates) is a viable route to second-order nonlinear optical materials.

CONCLUSIONS

Our method of preparing multilayers of metal-bis(phosphonates) via layer-by-layer growth involves the use of acentric bis(phosphonates) which are "protected" at one terminus and "functional" at the other. The functional terminus binds to Hf-primed SiO_2 surfaces, orienting the NLO chromophores. Gentle acid hydrolysis of the ester protection groups using 0.5 M HCl allows for subsequent metal deposition and the production of multilayers. This method was used to to produce regular multilayers on both Si and glass substrates with the azobenzene molecule I and Zr as the metal component. SHG results presented herein illustrate the expected increase in SH response with increasing number of layers on both Si and glass substrates, and thus show our method to be viable for producing thin film materials with second-order NLO properties.

Acknowledgments

Second harmonic generation (SHG) measurements were performed in collaboration with Dr. Derek Gragson and Dr. Heather Allen of the Richmond Lab and with the assistance of Dr. David Alavi, director of the Shared Laser Facility at the University of Oregon.

References

[1] H.E. Katz, W.L. Wilson and G. Scheller, *J. Am. Chem. Soc.*, **116**, 6636 (1994).
[2] W. Lin, W. Lin, G.K. Wong and T.J. Marks, *J. Am. Chem. Soc.*, **118**, 8034 (1996).
[3] P.N. Prasad and D.J. Williams, *Introduction* to *Nonlinear Optical Effects in Molecules and Polymers* (Wiley: New York, 1990).
[4] D. Li, M.A. Ratner, T.J. Marks, C. Zhang, J. Yang and G.K. Wong, *J. Am. Chem. Soc., 112,* 7389 (1990).
[5] W. Lin, S. Yitzchaik, W. Lin, A. Malik, M.K. Durbin, A.G. Richter, G.K. Wong, P. Dutta and T.J. Marks, *Angew. Chem. Int. Eng. Ed.*, **34**, 1497 (1995).
[6] D.G. Hanken, R.R. Naujok, J.M. Gray and R.M. Corn, *Anal. Chem.*, **69**, 240 (1997).
[7] G.A. Neff, T.M. Mahon, T.A. Abshere and C.J. Page, *Mater. Res. Soc. Symp. Proc.* **435**, 661 (1996).
[8] G.A. Neff, Ph.D. Dissertation, University of Oregon (1998).
[9] S. Yitzchaik, W. Lin, T.J. Marks, W. Lin and G.K. Wong, *Poly. Mat. Sci. Eng.*, **71**, 271 (1995).
[10] H.E. Katz, G.Scheller, T.M. Putvinski, M.L. Schilling, W.L. Wilson and C.E.D. Chidsey, *Science*, **254**, 1485 (1991).
[11] G.A. Neff, A.C. Zeppenfeld, B.J. Klopfenstein and C.J. Page, *Mater. Res. Soc. Symp. Proc.*, **351**, 269 (1994).
[12] A.C. Zeppenfeld, S.L. Fiddler, W.K. Ham, B.J. Klopfenstein and C.J. Page, *J. Amer. Chem. Soc.*, **116**, 9158 (1994).
[13] G.A. Neff, C.J. Page, E. Meintjes, T. Tsuda, W.-C. Pilgrim, N. Roberts and W.W. Warren, Jr., *Langmuir*, **12**, 238 (1996).