

**METAL–SEMICONDUCTOR TRANSITIONS IN NANOSCALE
VANADIUM DIOXIDE—THIN FILMS, SUBWAVELENGTH HOLES, AND
NANOPARTICLES**

By

Eugenii U. Donev

Dissertation

Submitted to the Faculty of the
Graduate School of Vanderbilt University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in

Physics

December 2008

Nashville, Tennessee

Approved:

Leonard C. Feldman

Richard F. Haglund, Jr.

Deyu Li

James H. Dickerson

Sharon M. Weiss

© Copyright by Eugenio U. Donev 2008
All Rights Reserved

CHAPTER V

CONFOCAL RAMAN MICROSCOPY ACROSS THE STRUCTURAL PHASE TRANSITION OF SINGLE VO₂ NANOPARTICLES

Abstract

The first Raman scattering measurements on nanoparticulate vanadium dioxide (VO₂) are presented here, as well as the first observations of the temperature-induced phase transition in *individual* VO₂ nanoparticles (NPs). We compare the Raman response of two VO₂ NPs and a companion VO₂ film undergoing their monoclinic-tetragonal-monoclinic transformations, and offer qualitative explanations for the large observed differences in hysteresis width. While bulk crystals and contiguous films contain numerous “potent” nucleation sites, individual NPs likely harbor only a few, which may make it possible to correlate detectable defects (*e.g.*, grain boundaries, dislocations) with the “ease” of switching phases as quantified by the width of the thermal hysteresis.

5.1 Introduction

Vanadium dioxide (VO₂), a transition-metal compound, has intrigued researchers for almost five decades since Morin²¹ first discovered its temperature-driven metal-insulator transition ($T_c \approx 67$ °C). Accompanying the electronic transition is a change in crystallographic structure, from monoclinic (insulator/semiconductor) below T_c to tetragonal/rutile (metal).^{22,23} The long-standing debate^{25–29} over the relative roles of lattice distortion and electron-electron correlation in the mechanism of the VO₂ phase transition has lately been reinvigorated, both theoretically^{30,55} and experimentally.^{1–3,31,32} Furthermore, the overall scientific drive towards understanding how materials behave on the nanoscale and, specifically, how phase transitions occur in nanocrystalline systems,^{10,16,37–39,41} has sparked in-

terest in making and probing nano-VO₂: thin films of nanosized grains^{3,45–49} or intertwined nanorods;^{190,191} thin films structured on silica microspheres¹⁰⁰ or perforated by nanoholes;¹⁴⁸ nanocrystalline powders;^{192,193} ensembles of implanted,^{50–52,54} grown,¹⁹⁴ or lithographically patterned nanoparticles (NPs).^{9,53} In the present work, we cross the next frontier by investigating the structural phase transition of *individual* VO₂ NPs, which paves the way to pinpointing the elusive sources of the VO₂ phase transition—those “potent” defect sites deemed responsible for nucleating the new phase inside the old.

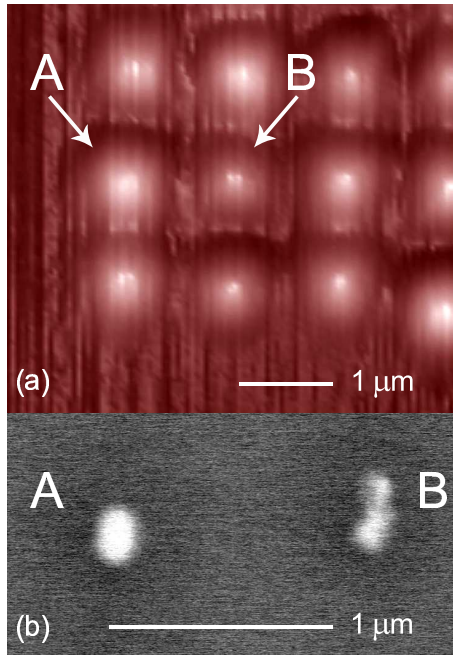


Figure 5.1: (a) Confocal image scan acquired at $\lambda = 633$ nm and (b) scanning electron micrograph (SEM) of VO₂ nanoparticles (NPs) on Si. Note the different morphologies of NP “A” and “B”.

Using confocal microscopy, we probed as a function of temperature the Raman response of two single VO₂ NPs (Figure 5.1) and a companion (“witness”) patch of contiguous VO₂ film, all on the same silicon (Si) substrate. This technique is well suited to interrogating structural changes in submicron particles because confocal scanning allows high-contrast imaging of an isolated NP, while Raman scattering identifies the lattice configuration of the

NP via the spectral signature of vibrational excitations. The Raman peaks of monoclinic and tetragonal VO_2 have been reported for bulk crystals and thin films;^{31,195–201} we present here the first Raman measurements on NPs of VO_2 (Figure 5.3). Monitoring the evolution of the Raman intensity with temperature furnished the hysteresis loops characteristic of the first-order phase transition of VO_2 , which proved much wider for the NPs than for the witness film (Figure 5.4). To explain the three different hysteresis widths observed in this study, we recall the model of heterogeneous nucleation of the VO_2 phase transition⁵ that accounted for the size-dependence of the hysteresis in ensembles of VO_2 NPs^{9,50} (see also Section 1.3.2).

5.2 Experimental details

We fabricated our VO_2 NPs on a Si substrate by means of: **(i)** focused-ion-beam lithography (FIB: 30-keV Ga^+ , 1-pA beam current, 100- μs dwell time per NP) in a spin-coated layer of poly(methyl-methacrylate) (PMMA: 50-nm thickness), followed by chemical removal of the exposed areas;^{9,53} **(ii)** pulsed-laser deposition (PLD: KrF excimer laser at $\lambda = 248$ nm, fluence $\approx 3 \text{ J}\cdot\text{cm}^{-2}$, V-metal target, O_2 gas at 5 mtorr) of amorphous, sub-stoichiometric vanadium oxide ($\text{VO}_{1.7}$, 30-nm thickness); **(iii)** chemical lift-off of the remaining PMMA and its $\text{VO}_{1.7}$ overlayer; **(iv)** thermal anneal (450 °C, O_2 gas at 250 mtorr) of the resulting arrays of $\text{VO}_{1.7}$ clusters to crystalline VO_2 NPs. This procedure has been demonstrated by multiple tests of stoichiometry, structure and switching properties to produce VO_2 rather than any of the multiple competing vanadium oxides.⁴⁵ The lattice constant of the NP array was chosen large enough, about 1 μm , to ensure that individual NPs could be resolved in a confocal image scan at the laser wavelength to be used for Raman measurements. One such scan is shown in Figure 5.1a, with arrows pointing to the two VO_2 NPs later probed as a function of temperature. Those NPs were selected because a scanning electron micrograph (SEM) had revealed clear differences in their morphology (Figure 5.1b), which we suspected might lead to different phase-transition behaviors. For comparison, we also measured the

Raman response of a “witness” patch of non-patterned VO₂ film on the same sample.

The sample was excited with a continuous-wave laser light (He-Ne: $\lambda = 633$ nm, 45 mW output power), fed through a monomode fiber into a scanning near-field optical microscope (SNOM) operating in confocal-reflection mode, then focused onto the sample with a micro-objective (60 X, NA = 0.80, $1/e^2$ beam spot ≈ 0.5 μm). The light scattered from the VO₂ NPs or witness film and the Si substrate was collected by the same micro-objective (backscattering geometry), filtered to reduce the elastic-scattering component, and sent through a multimode fiber to a spectrometer equipped with a cooled charge-coupled-device (CCD) detector. In order to minimize laser heating of the sample, the incident beam was attenuated before entering the microscope. The external sample temperature was controlled (± 0.5 °C) via a thermoelectric heater and a thermocouple attached to the substrate surface.

Raman measurements were performed at several fixed temperatures as follows: **(i)** the sample was manually positioned using micrometers to bring the approximate area of interest into the laser beam spot, as imaged onto a CCD camera under concurrent white-light illumination; **(ii)** the focus was visually adjusted by vertical displacement of the microscope head; **(iii)** the setup was then switched to confocal mode, whereby the piezoelectric sample stage would be scanned at increasing resolution and fine-adjusted laterally until the NP of interest occupied the center of a 2×2 - μm^2 image scan; **(iv)** as needed, the focus was also fine-tuned to yield a better object-to-substrate contrast; **(v)** finally, a 10-min Raman spectrum was collected. The sample was then heated up or cooled down, and the measurement sequence repeated at the next temperature point.

5.3 Results and discussion

5.3.1 Raman spectra

Figure 5.3 shows Raman spectra collected from the three VO₂-on-Si objects under investigation: witness film patch, misshapen particle “B”, and spheroidal particle “A”. The complete spectra (*e.g.*, see Figure 5.2) contain several peaks that match Stokes lines as-

signed in the literature to monoclinic VO₂ (*e.g.*, see Reference [201]), along with peaks belonging to the Si substrate (305 and 520 cm⁻¹). The peaks near 195 cm⁻¹ and 225

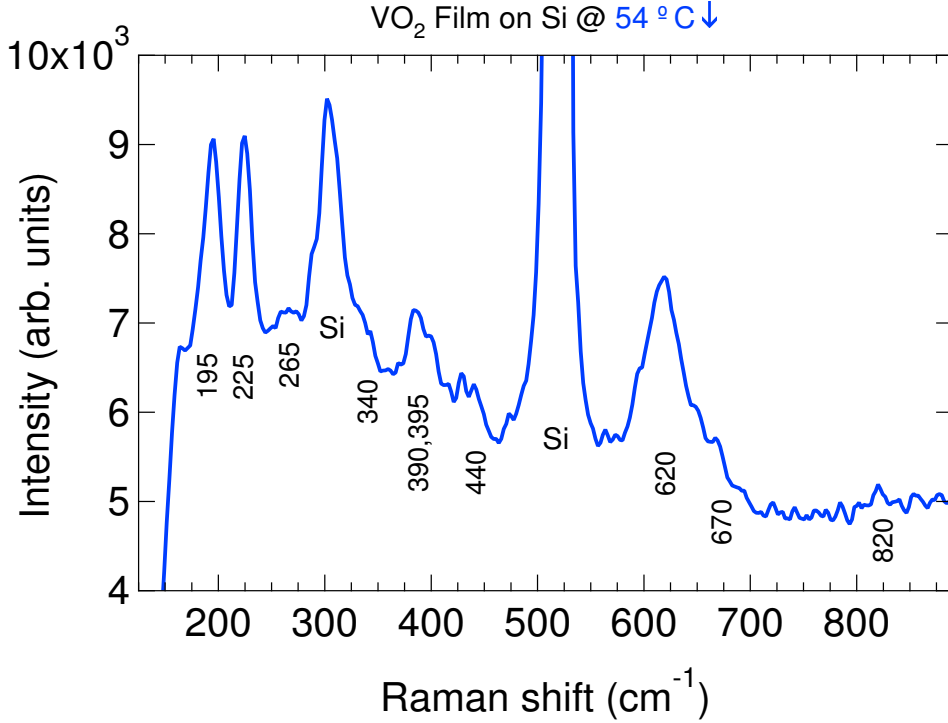


Figure 5.2: Representative Raman spectrum of the witness film in the monoclinic (low-temperature) phase, showing several characteristic VO₂ peaks and two Si-substrate peaks.

cm⁻¹ correspond to characteristic A_g -symmetry vibrational modes of the monoclinic (low-temperature) structure of VO₂, which vanish upon transition into the tetragonal (high-temperature) phase.^{195–197,201} These phonon modes play a crucial role in the structural transition of VO₂, since they are associated with the pairing and tilting motions of V–V dimers that map the monoclinic onto the tetragonal lattice configuration.³¹ In addition, the complete disappearance of the 195 cm⁻¹ peak at sufficiently high temperatures indicates that our VO₂ material does not contain measurable amounts of the V₂O₅ phase,¹⁹⁸ the terminal oxidation state of vanadium, which has a distinctive Raman line at 196 cm⁻¹.

Figure 5.3a presents snapshots of the temperature evolution of Raman intensity collected from each VO₂ object during heating of the sample towards the tetragonal phase. Only 2 °C above the bulk transition temperature of VO₂ (67 °C), the witness film no longer exhibits the monoclinic structure, as evidenced by the vanishing of the two A_g -peaks (top trace), which were present at room temperature (not shown). Similarly, NP “B” has also changed its structure, but not until a higher temperature of 75 °C (middle trace). Nanoparticle “A”, however, has retained the monoclinic signature even at 75 °C (bottom trace)—a clear thermal delay in the onset of its monoclinic-to-tetragonal transition with respect to the transitions of NP “B” and the witness film.

Raman spectra representative of the cooling half-cycle for each VO₂ object are shown in Figure 5.3b. The temperature was ramped down from a high-enough value to ensure completion of each object’s forward (monoclinic-to-tetragonal) transition. At 54 °C, the witness film has already reverted to the monoclinic phase (top trace), while the A_g -peaks for either NP have not yet reappeared (not shown). For NP “B”, they reappear by 46 °C (middle trace), but NP “A” remains tetragonal down to at least 33 °C (bottom trace). Thus, the onset of the reverse (tetragonal-to-monoclinic) transition of NP “A” is also delayed in temperature compared to the transitions of NP “B” and the witness film.

We note in passing that the Si peak at 305 cm⁻¹ diminishes slightly above the VO₂ phase transition, most likely because of the vanishing of an underlying peak of monoclinic VO₂, usually reported around 310 cm⁻¹.^{195,197-201}

5.3.2 Thermal hystereses of the Raman intensity

For each of the three VO₂ objects, Figure 5.4 reveals the full temperature evolution of the Raman response through the thermal hysteresis that accompanies the first-order phase transition. The data points correspond to the total Raman intensity in the spectral interval containing both VO₂ peaks, summed between 165 and 255 cm⁻¹ after background subtraction. The background was removed using an algorithm implementing a rolling-circle

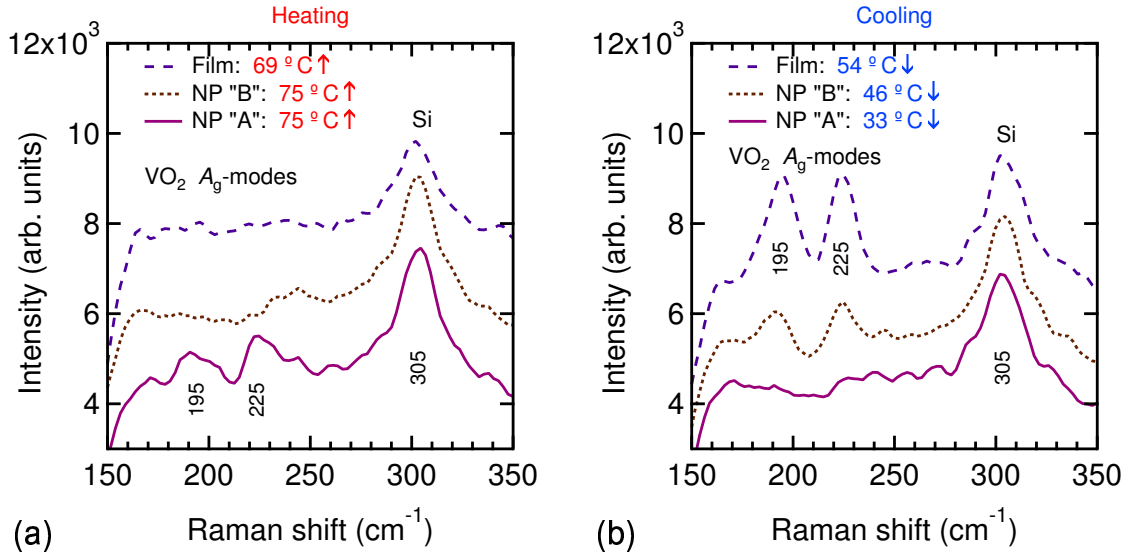


Figure 5.3: (a) During heating (\uparrow) towards the tetragonal (high-temperature) phase, the witness film and NP “B” complete the structural transition (A_g -modes vanish) before 69 and 75 °C, respectively, while NP “A” remains at least partly untransformed at 75 °C. (b) During cooling (\downarrow) from the high-temperature phase, NP “A” again lags thermally behind the film and NP “B” in switching back to the monoclinic phase.

spectral filter, which distinguishes between peaks and baselines according to their radii of curvature.²⁰² The comparatively large scatter in Figure 5.4b likely stems from a variable overlap between the laser beam spot and the irregular shape of NP “B” (Figure 5.1b) during different measurement sequences. The smooth lines through the data, used to estimate the transition mid-points (T_{half}) for the heating and cooling branches of each hysteresis loop, were obtained by least-squares fitting of an empirical sigmoidal function, the so-called Hill’s equation:

$$I(T) = I_{\text{base}} + (I_{\text{max}} - I_{\text{base}}) \left/ 1 + \left(\frac{T_{\text{half}}}{T} \right)^{\text{rate}} \right. . \quad (5.1)$$

This function is used for convenience, and is not meant to imply a physical significance.

The most striking features of the three hysteresis loops are their very different widths: from 2 ± 1 °C for the witness film (Figure 5.4a) to 18 ± 2 °C for NP “B” (Figure 5.4b) and 56 ± 5 °C for NP “A” (Figure 5.4c). In general, a first-order phase transformation requires

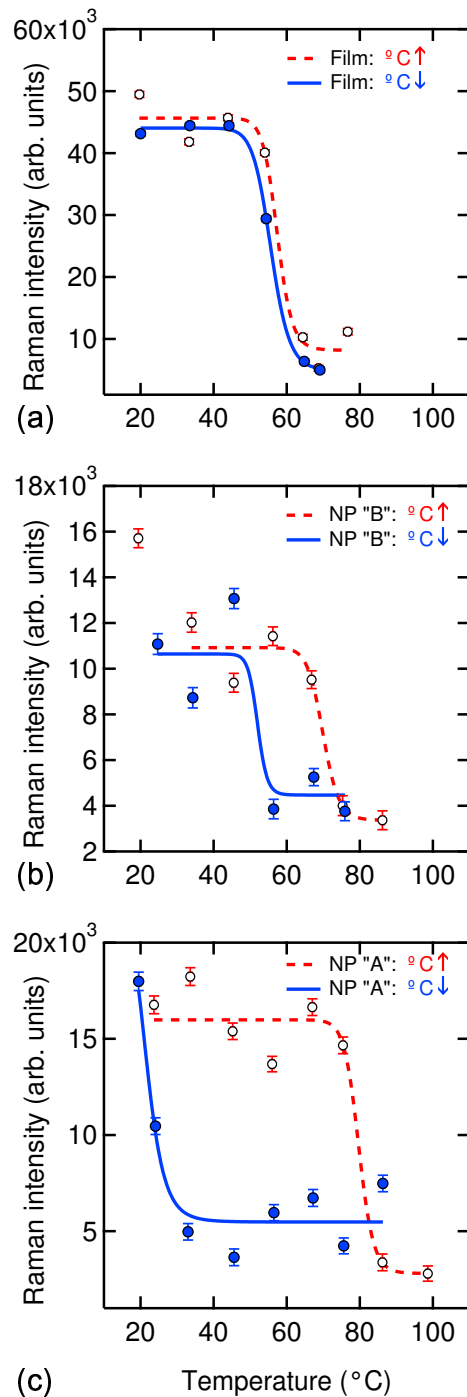


Figure 5.4: Thermal hystereses of the Raman intensity ($165\text{--}255\text{ cm}^{-1}$, minus background), for (a) witness film, (b) nanoparticle “B”, and (c) nanoparticle “A”. Dashed / solid fit line is for the heating (\uparrow) / cooling (\downarrow) half-cycle; one data point in (b) is excluded from the fit as an outlier; error bars indicate statistical uncertainty. The hysteresis width is a measure of the “ease” of switching between the low- and high-temperature states.

some amount of overheating above and undercooling below the equilibrium transition temperature, where the free-energy curves of the two phases intersect with a discontinuity in the first derivative (see Section 1.2). At thermodynamic equilibrium, the system occupies one of the two (meta)stable states depending on the transformation history, *i.e.*, whether the temperature has been increasing or decreasing. For example, martensitic structural transformations,⁷⁰ a class to which the VO₂ phase transition belongs,⁷⁵ take place at two constant temperatures when only a single interface between the two phases is involved (*e.g.*, in single crystals); however, the transition points may vary over a range of temperatures in materials with multiple interfaces, such as polycrystals.⁷²

Specifically for VO₂, the sharpness, shape, width, position, and switching ratio of the thermal hysteresis have been shown to depend critically on the quality of the VO₂ material (crystallinity, stoichiometry, impurities),^{45,95,203,204} grain size, distribution, and orientation,^{46,47,75,79,81} and NP size.^{5,9} Considering the statistical characteristics of heterogeneous nucleation of martensitic transformations,^{43,44} Lopez *et al.* have proposed an explanation of the increasingly wider hystereses (up to 50 °C) with decreasing NP sizes, as observed in near-infrared transmission through VO₂ NPs implanted into silica.⁵ According to the model, a small VO₂ particle has a certain probability of switching phases that depends, for any given temperature, on the availability of “potent defects”. These defects are envisioned as stochastically distributed sites where the free-energy barrier is low enough for the new phase to nucleate inside the parent phase. The probability of finding at least one such nucleation site per particle, and hence the probability of transformation, is modelled phenomenologically as a function of particle volume and the temperature-dependent excess driving force⁴⁴ (see also Section 1.3.2). A small amount of VO₂ material, such as our NP “A” or “B”, would require substantial overheating and undercooling beyond the nominal transition temperature (*i.e.*, excess driving forces) to change from the monoclinic to the tetragonal phase and *vice versa*, thereby exhibiting a wide thermal hysteresis (Figure 5.4b and 5.4c). On the other hand, a contiguous VO₂ film contains many nucleation sites due

to the large accessible volume, so that even relatively small excursions in temperature can initiate the phase transition, resulting in a narrower hysteresis loop (Figure 5.4a).

The above arguments help explain why the Raman hysteresis loops of our NPs are much wider than that of the witness film: The “ease” of switching depends on the presence of nucleation sites, which become more scarce as the volume of VO₂ material involved shrinks. But why is NP “B” much “easier” to switch than NP “A” ($\Delta T_B = 18 \pm 2$ °C *vs.* $\Delta T_A = 56 \pm 5$ °C) when both NPs should have the same volume, predetermined by lithographic and deposition conditions? Figure 5.1b offers a possible explanation. The evident differences in surface morphology may indicate that NP “A” constitutes one single-crystal grain, whereas NP “B” possibly contains grain boundaries, dislocations, or other structural imperfections as a result of the post-deposition annealing process, and those can act as potent sites for heterogeneous nucleation of the phase transition, thus yielding a narrower hysteresis for the more “defective” particle. Of course, without direct measurements of the underlying crystallinity of these specific NPs, such reasoning remains speculative though in keeping with the notion of the stochastic nature of the VO₂ phase transition, namely that NPs of a well-defined size do not have a unique T_c but a probability of switching centered at that temperature.⁹

5.4 Summary and outlook

To summarize, we reported the first observations of the phase transition in *individual* VO₂ NPs and the evolution of their Raman response as a function of temperature. In accord with previous results from ensembles of VO₂ NPs,^{5,9} the two single NPs studied here exhibited thermal hysteresis loops much wider than that of a companion thin film (Figure 5.4). In fact, NP “A” (Figure 5.1b) produced one of the widest VO₂ hystereses reported to date: $\Delta T_A = 56 \pm 5$ °C. Such large thermal delays in the monoclinic-tetragonal-monoclinic transition cycles for isolated nanoscale amounts of VO₂ have been attributed to the diminished availability of nucleation sites active at a given temperature as the volume of the

probed material decreases.⁵ Various stochastically occurring defects (vacancies, dislocations, untransformed embryonic regions, etc.) can become potent sites for heterogeneous nucleation, so even NPs of identical volumes may transform with different “ease”, that is, different hysteresis widths (Figure 5.4b *vs.* 5.4c).

The single-particle measurements reported here afford a direct way to obtain statistical information on the distribution of potent nucleation sites, namely by spatio-thermal confocal mapping of the Raman (or other optical) response of arrays of widely spaced VO₂ nanocrystals of a given nominal size. Armed with many single-NP hystereses and the corresponding particle morphologies or, better still, electron-diffraction patterns,^{3,36} one can gain valuable insight into the microscopic, “special-site” origins of the phase transition of this fascinating material.

REFERENCES

- [1] C. KÜBLER, H. EHRKE, R. HUBER, R. LOPEZ, A. HALABICA, R. F. HAGLUND, and A. LEITENSTORFER, *Physical Review Letters* **99**, 116401 (2007).
- [2] M. M. QAZILBASH, M. BREHM, B. G. CHAE, P. C. HO, G. O. ANDREEV, B. J. KIM, S. J. YUN, A. V. BALATSKY, M. B. MAPLE, F. KEILMANN, H. T. KIM, and D. N. BASOV, *Science* **318**, 1750 (2007).
- [3] P. BAUM, D. S. YANG, and A. H. ZEWAİL, *Science* **318**, 788 (2007).
- [4] A. SHARONI, J. G. RAMÍREZ, and I. K. SCHULLER, *Physical Review Letters* **101**, 026404 (2008).
- [5] R. LOPEZ, T. E. HAYNES, L. A. BOATNER, L. C. FELDMAN, and R. F. HAGLUND, *Physical Review B* **65**, 224113 (2002).
- [6] T. W. EBBESEN, H. J. LEZEC, H. F. GHAEMI, T. THIO, and P. A. WOLFF, *Nature* **391**, 667 (1998).
- [7] T. J. KIM, T. THIO, T. W. EBBESEN, D. E. GRUPP, and H. J. LEZEC, *Optics Letters* **24**, 256 (1999).
- [8] J. DINTINGER, A. DEGIRON, and T. W. EBBESEN, *MRS Bulletin* **30**, 381 (2005).
- [9] R. LOPEZ, L. C. FELDMAN, and R. F. HAGLUND, *Physical Review Letters* **93**, 177403 (2004).
- [10] C. X. WANG and G. W. YANG, *Materials Science & Engineering R: Reports* **49**, 157 (2005).
- [11] J. G. LEE and H. MORI, *Physical Review Letters* **93**, 235501 (2004).
- [12] K. K. NANDA, A. MAISELS, F. E. KRUIS, H. FISSAN, and S. STAPPERT, *Physical Review Letters* **91**, 106102 (2003).
- [13] T. SHIBATA, B. A. BUNKER, Z. Y. ZHANG, D. MEISEL, C. F. VARDEMAN, and J. D. GEZELTER, *Journal of the American Chemical Society* **124**, 11989 (2002).
- [14] T. SHINOHARA, T. SATO, and T. TANIYAMA, *Physical Review Letters* **91**, 197201 (2003).
- [15] H. J. MAMIN, R. BUDAKIAN, B. W. CHUI, and D. RUGAR, *Physical Review Letters* **91**, 207604 (2003).
- [16] K. DICK, T. DHANASEKARAN, Z. ZHANG, and D. MEISEL, *Journal of the American Chemical Society* **124**, 2312 (2002).
- [17] R. A. MASUMURA, P. M. HAZZLEDINE, and C. S. PANDE, *Acta Materialia* **46**, 4527 (1998).

- [18] D. KATZ, T. WIZANSKY, O. MILLO, E. ROTHENBERG, T. MOKARI, and U. BANIN, *Physical Review Letters* **89**, 199901 (2002).
- [19] J. T. LAU, A. FOHLISCH, R. NIETUBYC, M. REIF, and W. WURTH, *Physical Review Letters* **89**, 057201 (2002).
- [20] C. VOISIN, D. CHRISTOFILOS, N. D. FATTI, F. VALLEE, B. PREVEL, E. COTTANCIN, J. LERME, M. PELLARIN, and M. BROYER, *Physical Review Letters* **85**, 2200 (2000).
- [21] F. J. MORIN, *Physical Review Letters* **3**, 34 (1959).
- [22] J. B. GOODENOUGH, *Journal of Solid State Chemistry* **3**, 490 (1971).
- [23] M. IMADA, A. FUJIMORI, and Y. TOKURA, *Reviews of Modern Physics* **70**, 1039 (1998).
- [24] P. A. COX, *Transition metal oxides: An introduction to their electronic structure and properties*, The International Series of Monographs on Chemistry, Clarendon Press; Oxford University Press, Oxford New York, 1992.
- [25] A. ZYLBERSZTEJN and N. F. MOTT, *Physical Review B* **11**, 4383 (1975).
- [26] D. PAQUET and P. L. HUGON, *Physical Review B* **22**, 5284 (1980).
- [27] R. M. WENTZCOVITCH, W. W. SCHULZ, and P. B. ALLEN, *Physical Review Letters* **73**, 3043 (1994).
- [28] T. M. RICE, H. LAUNOIS, and J. P. POUGET, *Physical Review Letters* **73**, 3042 (1994).
- [29] R. M. WENTZCOVITCH, W. W. SCHULZ, and P. B. ALLEN, *Physical Review Letters* **72**, 3389 (1994).
- [30] S. BIERMANN, A. POTERYAEV, A. I. LICHTENSTEIN, and A. GEORGES, *Physical Review Letters* **94**, 026404 (2005).
- [31] A. CAVALLERI, T. DEKORSY, H. H. W. CHONG, J. C. KIEFFER, and R. W. SCHOENLEIN, *Physical Review B* **70**, 161102 (2004).
- [32] H. T. KIM, Y. W. LEE, B. J. KIM, B. G. CHAE, S. J. YUN, K. Y. KANG, K. J. HAN, K. J. YEE, and Y. S. LIM, *Physical Review Letters* **97**, 266401 (2006).
- [33] A. CAVALLERI, M. RINI, and R. W. SCHOENLEIN, *Journal of the Physical Society of Japan* **75**, 011004 (2006).
- [34] V. S. VIKHNIN, S. LYSENKO, A. RUA, F. FERNANDEZ, and H. LIU, *Solid State Communications* **137**, 615 (2006).
- [35] S. LYSENKO, A. J. RUA, V. VIKHNIN, J. JIMENEZ, F. FERNANDEZ, and H. LIU, *Applied Surface Science* **252**, 5512 (2006).
- [36] M. S. GRINOLDS, V. A. LOBASTOV, J. WEISSENRIEDER, and A. H. ZEWAIL, *Proceedings of the National Academy of Sciences of the United States of America* **103**, 18427 (2006).

- [37] I. YAMASHITA, H. KAWAJI, T. ATAKE, Y. KUROIWA, and A. SAWADA, *Physical Review B* **68**, 092104 (2003).
- [38] A. S. SHIRINYAN and M. WAUTELET, *Nanotechnology* **15**, 1720 (2004).
- [39] G. F. GOYA, M. VEITH, R. RAPALAVICUITE, H. SHEN, and S. MATHUR, *Applied Physics A: Materials Science & Processing* **80**, 1523 (2005).
- [40] K. JACOBS, J. WICKHAM, and A. P. ALIVISATOS, *Journal of Physical Chemistry B* **106**, 3759 (2002).
- [41] D. ZAZISKI, S. PRILLIMAN, E. C. SCHER, M. CASULA, J. WICKHAM, S. M. CLARK, and A. P. ALIVISATOS, *Nano Letters* **4**, 943 (2004).
- [42] Q. XU, I. D. SHARP, C. W. YUAN, D. O. YI, C. Y. LIAO, A. M. GLAESER, A. M. MINOR, J. W. BEEMAN, M. C. RIDGWAY, P. KLUTH, I. AGER, J. W., D. C. CHRZAN, and E. E. HALLER, *Physical Review Letters* **97**, 155701 (2006).
- [43] R. E. CECH and D. TURNBULL, *Journal of Metals* , 124 (1956).
- [44] I. W. CHEN, Y. H. CHIAO, and K. TSUZAKI, *Acta Metallurgica* **33**, 1847 (1985).
- [45] J. Y. SUH, R. LOPEZ, L. C. FELDMAN, and R. F. HAGLUND, *Journal of Applied Physics* **96**, 1209 (2004).
- [46] D. BRASSARD, S. FOURMAUX, M. JEAN-JACQUES, J. C. KIEFFER, and M. A. EL KHAKANI, *Applied Physics Letters* **87**, 051910 (2005).
- [47] R. A. ALIEV, V. N. ANDREEV, V. M. KAPRALOVA, V. A. KLIMOV, A. I. SOBOLEV, and E. B. SHADRIN, *Physics of the Solid State* **48**, 929 (2006).
- [48] J. ROZEN, R. LOPEZ, R. F. HAGLUND, and L. C. FELDMAN, *Applied Physics Letters* **88**, 081902 (2006).
- [49] K. NAGASHIMA, T. YANAGIDA, H. TANAKA, and T. KAWAI, *Journal of Applied Physics* **101**, 026103 (2007).
- [50] R. LOPEZ, L. A. BOATNER, T. E. HAYNES, R. F. HAGLUND, and L. C. FELDMAN, *Applied Physics Letters* **79**, 3161 (2001).
- [51] R. LOPEZ, L. A. BOATNER, T. E. HAYNES, L. C. FELDMAN, and R. F. HAGLUND, *Journal of Applied Physics* **92**, 4031 (2002).
- [52] R. LOPEZ, T. E. HAYNES, L. A. BOATNER, L. C. FELDMAN, and R. F. HAGLUND, *Optics Letters* **27**, 1327 (2002).
- [53] R. LOPEZ, J. Y. SUH, L. C. FELDMAN, and R. F. HAGLUND, *Symposium Proceedings of the Materials Research Society* **820**, R1.5 (2004).
- [54] M. RINI, A. CAVALLERI, R. W. SCHOENLEIN, R. LOPEZ, L. C. FELDMAN, R. F. HAGLUND, L. A. BOATNER, and T. E. HAYNES, *Optics Letters* **30**, 558 (2005).
- [55] V. EYERT, *Annalen der Physik* **11**, 650 (2002).

- [56] M. M. QAZILBASH, K. S. BURCH, D. WHISLER, D. SHREKENHAMER, B. G. CHAE, H. T. KIM, and D. N. BASOV, *Physical Review B* **74**, 205118 (2006).
- [57] H. W. VERLEUR, A. S. BARKER, and C. N. BERGLUND, *Physical Review* **172**, 788 (1968).
- [58] S. SHIN, S. SUGA, M. TANIGUCHI, M. FUJISAWA, H. KANZAKI, A. FUJIMORI, H. DAIMON, Y. UEDA, K. KOSUGE, and S. KACHI, *Physical Review B* **41**, 4993 (1990).
- [59] M. M. QAZILBASH, A. A. SCHAFGANS, K. S. BURCH, S. J. YUN, B. G. CHAE, B. J. KIM, H. T. KIM, and D. N. BASOV, *Physical Review B* **77**, 115121 (2008).
- [60] S. LYSENKO, V. VIKHNIN, F. FERNANDEZ, A. RUA, and H. LIU, *Physical Review B* **75**, 075109 (2007).
- [61] C. KITTEL, *Introduction to solid state physics*, Wiley, New York, 7th edition, 1996.
- [62] J. SPALEK, Superconductivity mechanisms, in *Encyclopedia of Modern Physics*, edited by R. A. MEYERS and S. N. SHORE, pp. 679–716, Academic Press, San Diego, 1990.
- [63] T. M. RICE and D. B. MCWHAN, *IBM Journal of Research and Development* **14**, 251 (1970).
- [64] N. F. MOTT, *Reviews of Modern Physics* **40**, 677 (1968).
- [65] J. HUBBARD, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **276**, 238 (1963).
- [66] A. I. BUZDIN and L. N. BULAYEVSKII, *Uspekhi Fizicheskikh Nauk* **131**, 495 (1980).
- [67] J. M. TOMCZAK and S. BIERMANN, *Journal of Physics: Condensed Matter* **19**, 365206 (2007).
- [68] M. W. HAVERKORT, Z. HU, A. TANAKA, W. REICHEL, S. V. STRELTSOV, M. A. KOROTIN, V. I. ANISIMOV, H. H. HSIEH, H. J. LIN, C. T. CHEN, D. I. KHOMSKII, and L. H. TJENG, *Physical Review Letters* **95**, 196404 (2005).
- [69] C. KÜBLER, H. EHRKE, A. LEITENSTORFER, R. LOPEZ, A. HALABICA, and R. F. HAGLUND, Ultrafast Conductivity and Lattice Dynamics of Insulator-Metal Phase Transition in VO₂ Studied via Multi-Terahertz Spectroscopy, in *Joint 31st Int'l Conference on Infrared and Millimeter Waves and 14th Int'l Conference on Terahertz Electronics (IRMMW-THz'06)*, Shanghai, China, 2006.
- [70] C. N. R. RAO and K. J. RAO, *Phase transitions in solids: an approach to the study of the chemistry and physics of solids*, McGraw-Hill, New York, 1978.
- [71] C. N. BERGLUND and H. J. GUGGENHEIM, *Physical Review* **185**, 1022 (1969).
- [72] J. ORTÍN, A. PLANES, and L. DELAEY, Hysteresis in Shape-Memory Materials, in *The Science of Hysteresis*, edited by G. BERTOTTI and I. D. MAYERGOYZ, volume 3, pp. 467–553, Elsevier, London, 2005.

- [73] L. DELAEY, Diffusionless Transformations, in *Phase Transformations in Materials*, edited by G. KOSTORZ, pp. 583–654, Wiley-VCH, Weinheim; New York; Chichester, new edition, 2001.
- [74] P. C. CLAPP, *Journal de Physique IV* **5**, 11 (1995).
- [75] I. A. KHAKHAEV, F. A. CHUDNOVSKII, and E. B. SHADRIN, *Fizika Tverdogo Tela* **36**, 1643 (1994).
- [76] H. S. CHOI, J. S. AHN, J. H. JUNG, T. W. NOH, and D. H. KIM, *Physical Review B* **54**, 4621 (1996).
- [77] F. J. PEREZ-RECHE, E. VIVES, L. MANOSA, and A. PLANES, *Physical Review Letters* **8719**, 195701 (2001).
- [78] D. MAURER, A. LEUE, R. HEICHELE, and V. MÜLLER, *Physical Review B* **60**, 13249 (1999).
- [79] J. NARAYAN and V. M. BHOSLE, *Journal of Applied Physics* **100**, 103524 (2006).
- [80] L. A. L. DE ALMEIDA, G. S. DEEP, A. M. N. LIMA, H. F. NEFF, and R. C. S. FREIRE, *Ieee Transactions on Instrumentation and Measurement* **50**, 1030 (2001).
- [81] V. A. KLIMOV, I. O. TIMOFEEVA, S. D. KHANIN, E. B. SHADRIN, A. V. ILINSKII, and F. SILVA-ANDRADE, *Technical Physics* **47**, 1134 (2002).
- [82] R. A. ALIEV and V. A. KLIMOV, *Physics of the Solid State* **46**, 532 (2004).
- [83] R. A. ALIEV, V. N. ANDREEV, V. A. KLIMOV, V. M. LEBEDEV, S. E. NIKITIN, E. I. TERUKOV, and E. B. SHADRIN, *Technical Physics* **50**, 754 (2005).
- [84] W. HAIDINGER and D. GROSS, *Thin Solid Films* **12**, 433 (1972).
- [85] Y. MURAOKA and Z. HIROI, *Applied Physics Letters* **80**, 583 (2002).
- [86] G. XU, P. JIN, M. TAZAWA, and K. YOSHIMURA, *Applied Surface Science* **244**, 449 (2005).
- [87] E. KUSANO and J. A. THEIL, *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films* **7**, 1314 (1989).
- [88] V. A. KLIMOV, I. O. TIMOFEEVA, S. D. KHANIN, E. B. SHADRIN, A. V. IL'INSKII, and F. SILVA-ANDRADE, *Semiconductors* **37**, 370 (2003).
- [89] F. BETEILLE and J. LIVAGE, *Journal of Sol-Gel Science and Technology* **13**, 915 (1998).
- [90] W. BURKHARDT, T. CHRISTMANN, B. K. MEYER, W. NIESSNER, D. SCHALCH, and A. SCHARMANN, *Thin Solid Films* **345**, 229 (1999).
- [91] E. CAVANNA, J. P. SEGAUD, and J. LIVAGE, *Materials Research Bulletin* **34**, 167 (1999).
- [92] F. C. CASE, *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films* **2**, 1509 (1984).

- [93] F. C. CASE, *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films* **7**, 1194 (1989).
- [94] A. LEONE, A. M. TRIONE, and F. JUNGA, *IEEE Transactions on Nuclear Science* **37**, 1739 (1990).
- [95] P. JIN, S. NAKAO, and S. TANEMURA, *Nuclear Instruments & Methods in Physics B: Beam Interactions with Materials & Atoms* **141**, 419 (1998).
- [96] L. B. LIN, T. C. LU, Q. LIU, Y. LU, and X. D. FENG, *Surface & Coatings Technology* **158**, 530 (2002).
- [97] F. BETEILLE, L. MAZEROLLES, and J. LIVAGE, *Materials Research Bulletin* **34**, 2177 (1999).
- [98] C. PETIT, J. M. FRIGERIO, and M. GOLDMANN, *Journal of Physics-Condensed Matter* **11**, 3259 (1999).
- [99] K. Y. TSAI, T. S. CHIN, H. P. D. SHIEH, and C. H. MA, *Journal of Materials Research* **19**, 2306 (2004).
- [100] I. KARAKURT, J. BONEBERG, P. LEIDERER, R. LOPEZ, A. HALABICA, and R. F. HAGLUND, *Applied Physics Letters* **91**, 091907 (2007).
- [101] J. E. MAHAN, *Physical vapor deposition of thin films*, Wiley, New York; Chichester, 2000.
- [102] O. SVELTO, S. LONGHI, G. D. VALLE, S. KÜCK, G. HUBER, M. POLLNAU, and H. HILLMER ETC., Lasers and Coherent Light Sources, in *Springer Handbook of Lasers and Optics*, edited by F. TRÄGER, pp. 583–936, Springer, New York, 2007.
- [103] N. D. BASSIM, P. K. SCHENCK, E. U. DONEV, E. J. HEILWEIL, E. COCKAYNE, M. L. GREEN, and L. C. FELDMAN, *Applied Surface Science* **254**, 785 (2007).
- [104] C. A. VOLKERT and A. M. MINOR, *MRS Bulletin* **32**, 389 (2007).
- [105] P. RAI-CHOUDHURY, *Handbook of Microlithography, Micromachining, and Microfabrication*, volume 1, SPIE Optical Engineering Press; Institution of Electrical Engineers, Bellingham, Wash., USA London, UK, 1997.
- [106] T. L. ALFORD, L. C. FELDMAN, and J. W. MAYER, *Fundamentals of nanoscale film analysis*, Springer, New York; London, 2007.
- [107] M. MAYER, *SIMNRA (ver. 5.02)*, <http://www.ipp.mpg.de/~mam>, 2004.
- [108] K. IIZUKA, *Elements of photonics*, Wiley Series in Pure and Applied Optics, Wiley, New York, 2002.
- [109] WITec, *AlphaSNOM Manual*, WITec Wissenschaftliche Instrumente und Technologie GmbH, 2002.
- [110] M. FOX, *Optical properties of solids*, Oxford Master Series in Condensed Matter Physics, Oxford University Press, Oxford; New York, 2001.

- [111] G. BROOKER, *Modern classical optics*, Oxford University Press, Oxford, 2003.
- [112] L. NOVOTNY and B. HECHT, *Principles of Nano-Optics*, Cambridge University Press, 2006.
- [113] S. A. MAIER and H. A. ATWATER, *Journal of Applied Physics* **98**, 011101 (2005).
- [114] U. KREIBIG, M. GARTZ, A. HILGER, and H. HOVEL, *Optical investigations of surfaces and interfaces of metal clusters*, volume 4, JAI Press, Inc., Stanford, 1998.
- [115] K. L. KELLY, E. CORONADO, L. L. ZHAO, and G. C. SCHATZ, *Journal of Physical Chemistry B* **107**, 668 (2003).
- [116] J. D. JACKSON, *Classical electrodynamics*, Wiley, New York, 3rd edition, 1999.
- [117] M. L. SANDROCK and C. A. FOSS, *Journal of Physical Chemistry B* **103**, 11398 (1999).
- [118] G. MIE, *Annalen der Physik* **25**, 377 (1908).
- [119] I. W. SUDIARTA and P. CHYLEK, *Journal of the Optical Society of America A* **18**, 1275 (2001).
- [120] H. C. VAN DE HULST, *Light Scattering by Small Particles*, Dover Publications, Inc., New York, 1981.
- [121] M. B. CORTIE, A. DOWD, N. HARRIS, and M. J. FORD, *Physical Review B* **75**, 113405 (2007).
- [122] L. R. HIRSCH, R. J. STAFFORD, J. A. BANKSON, S. R. SERSHEN, B. RIVERA, R. E. PRICE, J. D. HAZLE, N. J. HALAS, and J. L. WEST, *Proceedings of the National Academy of Sciences of the United States of America* **100**, 13549 (2003).
- [123] J. M. BROCKMAN, B. P. NELSON, and R. M. CORN, *Annual Review of Physical Chemistry* **51**, 41 (2000).
- [124] E. U. DONEV, J. Y. SUH, F. VILLEGAS, R. LOPEZ, R. F. HAGLUND, and L. C. FELDMAN, *Physical Review B* **73**, 201401 (2006).
- [125] J. Y. SUH, E. U. DONEV, R. LOPEZ, L. C. FELDMAN, and R. F. HAGLUND, *Applied Physics Letters* **88**, 133115 (2006).
- [126] A. BIANCONI, S. STIZZA, and R. BERNARDINI, *Physical Review B* **24**, 4406 (1981).
- [127] Y. N. XIA and N. J. HALAS, *MRS Bulletin* **30**, 338 (2005).
- [128] G. XU, Y. CHEN, M. TAZAWA, and P. JIN, *Journal of Physical Chemistry B* **110**, 2051 (2006).
- [129] E. A. CORONADO and G. C. SCHATZ, *Journal of Chemical Physics* **119**, 3926 (2003).
- [130] M. MAAZA, O. NEMRAOUI, C. SELLA, A. C. BEYE, and B. BARUCH-BARAK, *Optics Communications* **254**, 188 (2005).

- [131] W. RECHBERGER, A. HOHENAU, A. LEITNER, J. R. KRENN, B. LAMPRECHT, and F. R. AUSSENEKG, *Optics Communications* **220**, 137 (2003).
- [132] J. Y. SUH, E. U. DONEV, D. W. FERRARA, K. A. TETZ, L. C. FELDMAN, and R. F. HAGLUND, *Journal of Optics A: Pure and Applied Optics* , 055202 (2008).
- [133] M. D. MCMAHON, R. LOPEZ, R. F. HAGLUND, E. A. RAY, and P. H. BUNTON, *Physical Review B* **73**, 041401 (2006).
- [134] S. WANG, D. F. P. PILE, C. SUN, and X. ZHANG, *Nano Letters* **7**, 1076 (2007).
- [135] C. A. FOSS, G. L. HORNYAK, J. A. STOCKERT, and C. R. MARTIN, *Journal of Physical Chemistry* **98**, 2963 (1994).
- [136] J. GRAND, P. M. ADAM, A. S. GRIMAULT, A. VIAL, M. L. DE LA CHAPELLE, J. L. BIJEON, S. KOSTCHEEV, and P. ROYER, *Plasmonics* **1**, 135 (2006).
- [137] K. H. SU, Q. H. WEI, X. ZHANG, J. J. MOCK, D. R. SMITH, and S. SCHULTZ, *Nano Letters* **3**, 1087 (2003).
- [138] T. R. JENSEN, M. L. DUVAL, K. L. KELLY, A. A. LAZARIDES, G. C. SCHATZ, and R. P. VAN DUYN, *Journal of Physical Chemistry B* **103**, 9846 (1999).
- [139] J. J. MOCK, D. R. SMITH, and S. SCHULTZ, *Nano Letters* **3**, 485 (2003).
- [140] P. B. JOHNSON and R. W. CHRISTY, *Physical Review B* **6**, 4370 (1972).
- [141] S. LINK and M. A. EL-SAYED, *Journal of Physical Chemistry B* **103**, 4212 (1999).
- [142] H. BETHE, *Physical Review* **66**, 163 (1944).
- [143] C. J. BOUWKAMP, *IEEE Transactions on Antennas and Propagation* **AP18**, 152 (1970).
- [144] H. LIU and P. LALANNE, *Nature* **452**, 728 (2008).
- [145] C. LIU, V. KAMAEV, and Z. V. VARDENY, *Applied Physics Letters* **86**, 143501 (2005).
- [146] A. KRISHNAN, T. THIO, T. J. KIMA, H. J. LEZEC, T. W. EBBESEN, P. A. WOLFF, J. PENDRY, L. MARTIN-MORENO, and F. J. GARCIA-VIDAL, *Optics Communications* **200**, 1 (2001).
- [147] E. HENDRY, M. J. LOCKYEAR, J. GÓMEZ-RIVAS, L. KUIPERS, and M. BONN, *Physical Review B* **75**, 235305 (2007).
- [148] E. U. DONEV, J. Y. SUH, R. LOPEZ, L. C. FELDMAN, and R. F. HAGLUND, *Advances in OptoElectronics* , 739135 (2008).
- [149] S. G. TIKHODEEV, A. L. YABLONSKII, E. A. MULJAROV, N. A. GIPPIUS, and T. ISHIHARA, *Physical Review B* **66**, 045102 (2002).
- [150] A. ROBERTS, *Journal of the Optical Society of America A: Optics Image Science and Vision* **4**, 1970 (1987).

- [151] A. LIEBSCH, *Physical Review Letters* **71**, 145 (1993).
- [152] W. L. BARNES, *Journal of Optics A: Pure and Applied Optics* **8**, S87 (2006).
- [153] H. RAETHER, *Springer Tracts in Modern Physics* **111**, 1 (1988).
- [154] W. L. BARNES, A. DEREUX, and T. W. EBBESEN, *Nature* **424**, 824 (2003).
- [155] A. V. ZAYATS, L. SALOMON, and F. DE FORNEL, *Journal of Microscopy* **210**, 344 (2003).
- [156] H. F. GHAEMI, T. THIO, D. E. GRUPP, T. W. EBBESEN, and H. J. LEZEC, *Physical Review B* **58**, 6779 (1998).
- [157] D. S. KIM, S. C. HOHNG, V. MALYARCHUK, Y. C. YOON, Y. H. AHN, K. J. YEE, J. W. PARK, J. KIM, Q. H. PARK, and C. LIENAU, *Physical Review Letters* **91**, 143901 (2003).
- [158] P. LALANNE, J. C. RODIER, and J. P. HUGONIN, *Journal of Optics A: Pure and Applied Optics* **7**, 422 (2005).
- [159] E. POPOV, M. NEVIERE, S. ENOCH, and R. REINISCH, *Physical Review B* **62**, 16100 (2000).
- [160] S. ENOCH, E. POPOV, M. NEVIERE, and R. REINISCH, *Journal of Optics A: Pure and Applied Optics* **4**, S83 (2002).
- [161] T. THIO, H. F. GHAEMI, H. J. LEZEC, P. A. WOLFF, and T. W. EBBESEN, *Journal of the Optical Society of America B: Optical Physics* **16**, 1743 (1999).
- [162] L. MARTIN-MORENO, F. J. GARCIA-VIDAL, H. J. LEZEC, K. M. PELLERIN, T. THIO, J. B. PENDRY, and T. W. EBBESEN, *Physical Review Letters* **86**, 1114 (2001).
- [163] S. A. DARMANYAN and A. V. ZAYATS, *Physical Review B* **67**, 035424 (2003).
- [164] W. L. BARNES, W. A. MURRAY, J. DINTINGER, E. DEVAUX, and T. W. EBBESEN, *Physical Review Letters* **92**, 107401 (2004).
- [165] H. J. LEZEC and T. THIO, *Optics Express* **12**, 3629 (2004).
- [166] G. GAY, O. ALLOSCHERY, B. V. DE LESEGNO, C. O'DWYER, J. WEINER, and H. J. LEZEC, *Nature Physics* **2**, 262 (2006).
- [167] G. GAY, O. ALLOSCHERY, B. V. DE LESEGNO, J. WEINER, and H. J. LEZEC, *Physical Review Letters* **96**, 213901 (2006).
- [168] G. GAY, O. ALLOSCHERY, J. WEINER, H. J. LEZEC, C. O'DWYER, M. SUKHAREV, and T. SEIDEMAN, *Physical Review E* **75**, 016612 (2007).
- [169] P. LALANNE and J. P. HUGONIN, *Nature Physics* **2**, 551 (2006).
- [170] F. KALKUM, G. GAY, O. ALLOSCHERY, J. WEINER, H. J. LEZEC, Y. XIE, and M. MANSURIPUR, *Optics Express* **15**, 2613 (2007).

- [171] G. GAY, O. ALLOSCHERY, J. WEINER, H. J. LEZEC, C. O'DWYER, M. SUKHAREV, and T. SEIDEMAN, *Nature Physics* **2**, 792 (2006).
- [172] F. J. GARCIA-VIDAL, S. G. RODRIGO, and L. MARTIN-MORENO, *Nature Physics* **2**, 790 (2006).
- [173] P. LALANNE, J. P. HUGONIN, M. BESBES, and P. BIENSTMAN, *Nature Physics* **2**, 792 (2006).
- [174] J. WEINER and H. J. LEZEC, *Nature Physics* **2**, 791 (2006).
- [175] A. DEGIRON and T. W. EBBESEN, *Journal of Optics A: Pure and Applied Optics* **7**, S90 (2005).
- [176] C. GENET, M. P. VAN EXTER, and J. P. WOERDMAN, *Optics Communications* **225**, 331 (2003).
- [177] M. SARRAZIN and J. P. VIGNERON, *Physical Review E* **68**, 016603 (2003).
- [178] M. SARRAZIN, J. P. VIGNERON, and J. M. VIGOUREUX, *Physical Review B* **67**, 085415 (2003).
- [179] A. DEGIRON, H. J. LEZEC, W. L. BARNES, and T. W. EBBESEN, *Applied Physics Letters* **81**, 4327 (2002).
- [180] K. L. VAN DER MOLEN, F. B. SEGERINK, N. F. VAN HULST, and L. KUIPERS, *Applied Physics Letters* **85**, 4316 (2004).
- [181] A. HESSEL and A. A. OLINER, *Applied Optics* **4**, 1275 (1965).
- [182] F. J. GARCIA DE ABAJO, *Reviews of Modern Physics* **79**, 1267 (2007).
- [183] J. E. STEWART and W. S. GALLAWAY, *Applied Optics* **1**, 421 (1962).
- [184] E. D. PALIK, *Handbook of optical constants of solids*, Academic Press Handbook Series, Academic Press, Orlando, 1985.
- [185] W. BOGAERTS, P. BIENSTMAN, D. TAILLAERT, R. BAETS, and D. DE ZUTTER, *IEEE Photonics Technology Letters* **13**, 565 (2001).
- [186] A. DEGIRON, H. J. LEZEC, N. YAMAMOTO, and T. W. EBBESEN, *Optics Communications* **239**, 61 (2004).
- [187] A. CAVALLERI, C. TÓTH, C. W. SIDERS, J. A. SQUIER, F. RÁKSI, P. FORGET, and J. C. KIEFFER, *Physical Review Letters* **87**, 237401 (2001).
- [188] M. F. BECKER, A. B. BUCKMAN, R. M. WALSER, T. LEPINE, P. GEORGES, and A. BRUN, *Applied Physics Letters* **65**, 1507 (1994).
- [189] M. F. BECKER, A. B. BUCKMAN, R. M. WALSER, T. LEPINE, P. GEORGES, and A. BRUN, *Journal of Applied Physics* **79**, 2404 (1996).
- [190] K. C. KAM and A. K. CHEETHAM, *Materials Research Bulletin* **41**, 1015 (2006).

- [191] J. PARK, I. H. OH, E. LEE, K. W. LEE, C. E. LEE, K. SONG, and Y. J. KIM, *Applied Physics Letters* **91**, 153112 (2007).
- [192] F. GUINETON, L. SAUQUES, J. C. VALMALETTE, F. CROS, and J. R. GAVARRI, *Journal of Physics and Chemistry of Solids* **62**, 1229 (2001).
- [193] S. Q. XU, H. P. MA, S. X. DAI, and Z. H. JIANG, *Journal of Materials Science* **39**, 489 (2004).
- [194] S. A. PAULI, R. HERGER, P. R. WILLMOTT, E. U. DONEV, J. Y. SUH, and R. F. HAGLUND, *Journal of Applied Physics* **102**, 073527 (2007).
- [195] K. HYUN-TAK, C. BYUNG-GYU, Y. DOO-HYEB, K. GYUNGOCK, K. KWANG-YONG, L. SEUNG-JOON, K. KWAN, and L. YONG-SIK, *Applied Physics Letters* **86**, 242101 (2005).
- [196] R. SRIVASTAVA and L. L. CHASE, *Physical Review Letters* **27**, 727 (1971).
- [197] M. PAN, J. LIU, H. M. ZHONG, S. W. WANG, Z. F. LI, X. H. CHEN, and W. LU, *Journal of Crystal Growth* **268**, 178 (2004).
- [198] G. I. PETROV, V. V. YAKOVLEV, and J. SQUIER, *Applied Physics Letters* **81**, 1023 (2002).
- [199] J. C. PARKER, *Physical Review B* **42**, 3164 (1990).
- [200] H.-T. YUAN, K.-C. FENG, X.-J. WANG, C. LI, C.-J. HE, and Y.-X. NIE, *Chinese Physics* , 82 (2004).
- [201] P. SCHILBE, *Physica B: Condensed Matter* **316**, 600 (2002).
- [202] N. N. BRANDT, O. O. BROVKO, A. Y. CHIKISHEV, and O. D. PARASCHUK, *Applied Spectroscopy* **60**, 288 (2006).
- [203] C. H. GRIFFITHS and H. K. EASTWOOD, *Journal of Applied Physics* **45**, 2201 (1974).
- [204] C. L. XU, X. MA, X. LIU, W. Y. QIU, and Z. X. SU, *Materials Research Bulletin* **39**, 881 (2004).
- [205] D. DRAGOMAN and M. DRAGOMAN, *Optical characterization of solids*, Springer, Berlin; New York, 2002.
- [206] R. R. ANDRONENKO, I. N. GONCHARUK, V. Y. DAVYDOV, F. A. CHUDNOVSKII, and E. B. SHADRIN, *Physics of the Solid State* **36**, 1136 (1994).
- [207] P. SCHILBE and D. MAURER, *Materials Science and Engineering A: Structural Materials Properties Microstructure and Processing* **370**, 449 (2004).
- [208] H. H. RICHARDSON, Z. N. HICKMAN, A. O. GOVOROV, A. C. THOMAS, W. ZHANG, and M. E. KORDESCH, *Nano Letters* **6**, 783 (2006).
- [209] A. O. GOVOROV, W. ZHANG, T. SKEINI, H. RICHARDSON, J. LEE, and N. A. KOTOV, *Nanoscale Research Letters* **1**, 84 (2006).

- [210] G. A. THOMAS, D. H. RAPKINE, S. A. CARTER, A. J. MILLIS, T. F. ROSENBAUM, P. METCALF, and J. M. HONIG, *Physical Review Letters* **73**, 1529 (1994).
- [211] S. YONEZAWA, Y. MURAOKA, Y. UEDA, and Z. HIROI, *Solid State Communications* **129**, 245 (2004).
- [212] F. C. CASE, *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films* **9**, 461 (1991).
- [213] H. SCHULER, S. GRIGORIEV, and S. HORN, *Materials Research Society Symposium Proceedings* **474**, 291 (1997).
- [214] B. SASS, C. TUSCHE, W. FELSCH, N. QUAAS, A. WEISMANN, and M. WENDEROTH, *Journal of Physics: Condensed Matter* **16**, 77 (2004).
- [215] P. A. METCALF, S. GUHA, L. P. GONZALEZ, J. O. BARNES, E. B. SLAMOVICH, and J. M. HONIG, *Thin Solid Films* **515**, 3421 (2007).
- [216] D. B. MCWHAN and J. P. REMEIKA, *Physical Review B* **2**, 3734 (1970).
- [217] D. B. MCWHAN, A. JAYARAMAN, J. P. REMEIKA, and T. M. RICE, *Physical Review Letters* **34**, 547 (1975).
- [218] P. PFALZER, G. OBERMEIER, M. KLEMM, S. HORN, and M. L. DENBOER, *Physical Review B* **73**, 144106 (2006).
- [219] S. GUIMOND, M. ABU HALJA, S. KAYA, J. LU, J. WEISSENRIEDER, S. SHAIKHUTDINOV, H. KUHLENBECK, H. J. FREUND, J. DOBLER, and J. SAUER, *Topics in Catalysis* **38**, 117 (2006).
- [220] Y. JIANG, S. DECKER, C. MOHS, and K. J. KLABUNDE, *Journal of Catalysis* **180**, 24 (1998).
- [221] N. PINNA, M. ANTONIETTI, and M. NIEDERBERGER, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **250**, 211 (2004).
- [222] C. V. RAMANA, S. UTSUNOMIYA, R. C. EWING, and U. BECKER, *Solid State Communications* **137**, 645 (2006).
- [223] Z. H. YANG, P. J. CAI, L. Y. CHEN, Y. L. GU, L. SHI, A. W. ZHAO, and Y. T. QIAN, *Journal of Alloys and Compounds* **420**, 229 (2006).
- [224] K. F. ZHANG, J. S. GUO, C. H. TAO, X. LIU, H. L. LI, and Z. X. SU, *Chinese Journal of Inorganic Chemistry* **21**, 1090 (2005).
- [225] K. F. ZHANG, X. Z. SUN, G. W. LOU, X. LIU, H. L. LI, and Z. X. SU, *Materials Letters* **59**, 2729 (2005).