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Shaping nanoparticles and their optical spectra with photons

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Abstract. An experimental method to tailor the shape and the optical absorption spectra of metallic nanoparticles is presented. It exploits the influence of laser irradiation on particle growth by self-assembly of atoms deposited on a substrate surface. By applying nanosecond light pulses of appropriate fluence and three different wavelengths, oblate silver particles with three fixed axial ratios have been fabricated. Their optical extinction spectra were measured with s- and p-polarized light and are dominated by plasmon resonances at fixed photon energies determined by the axial ratio. Possible applications of such tailormade nanoclusters include catalytic converters and optical components with narrow-band extinction, the magnitude and center frequency of which can be specified in advance.

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Nanoparticles, or, more generally speaking, structures with dimensions in the nanometer regime, have been studied extensively in recent years. These systems have electronic, magnetic, optical and chemical properties which differ considerably from those of the corresponding bulk material and depend strongly on the size and the morphology of the structures under investigation [1–3]. In particular, nanoparticles of well-defined dimensions embedded in matrices or supported on substrate surfaces are therefore promising candidates for a variety of future applications. Examples are optical filters which selectively block radiation in narrow wavelength intervals, integrated optical devices for ultrafast switching of light [4] and improved catalytic converters featuring enhanced yield and selectivity [5, 6]. Unfortunately, however, the size- and shape-dependent characteristics of nanoparticles are often obscured by broad size and shape distributions that are typical of most production techniques and make it difficult, if not impossible, to exploit the unique properties of the generated aggregates. Recently, we demonstrated a novel method for fabricating *monodisperse* metal nanoclusters, i.e. particles of almost equal size, on dielectric substrates [7]. Even though development of this technique represents a major breakthrough, control of the *shape* of the particles independent of their size has remained a great challenge. Progress in developing such methods, however, is highly desirable since many properties of metal clusters depend not only on their size but also on their shape. In particular if particles are grown on a substrate surface by deposition of atoms, the shape may vary considerably. It depends strongly on the diffusion coefficients of the metal atoms on the substrate and on the surface of the growing clusters [8–10]. In general, one-, two- or three-dimensional islands and fractal aggregates can be formed, the actual shape depending on growth parameters such as the substrate temperature and the flux of atoms [8]. Brune, Kern and coworkers [8, 11, 12] have shown that the dependence of the shape on the growth parameters, can, if investigated in detail, be exploited for controlled generation of metallic aggregates with desired size and shape. In many cases, however, the complex interplay between the growth parameters and the resulting morphologies is a drawback rather than an advantage. Usually, simultaneous change of the mean size and shape of the nanostructures is observed [9, 13, 14]. For example, metal particles prepared at relatively low substrate temperatures become more and more oblate if the size increases, an effect which is even more pronounced if coalescence plays a role in the growth process.

Here, we present a new method to precisely and independently control the mean shape and the average diameter of nanoclusters prepared by self-assembly of atoms on dielectric substrates.

1 Generation and characterization of nanoclusters

Before we describe our method to control the shape of metal nanoparticles, we will first outline their preparation and characterization and explain how their shape is determined.

1.1 Generation of metal nanoparticles

In our experiments Ag atoms generated by an electron beam evaporator are deposited under ultrahigh vacuum conditions on quartz substrates, where they form three-dimensional

islands by diffusion and nucleation, i.e. Volmer–Weber growth. The coverage of Ag atoms is determined with a quartz crystal microbalance. It is well known that particles generated by this method usually exhibit broad size distributions and, if fabricated at temperatures lower then the barrier for self-diffusion, are aspherical [9, 13, 14]. The actual shape can be approximated by rotational ellipsoids with two main half-axes a and b; see Figure 1a.

1.2 Determination of the mean particle size

The particles are analyzed in situ by scanning force microscopy (SFM) to determine the number density and the mean size and by recording their optical extinction spectra in order to determine the average axial ratio a/b. An example of SFM measurements is shown in Figure 1b. Deposition of 2.3×10^{15} atoms/cm^2 which corresponds to an integral coverage of 4 monolayers (ML) leads to particles with a number density of 2×10^{12} /cm^2. The SFM images give a mean cluster height (measured in the direction of the substrate surface normal) of $\langle a \rangle = 1.8$ nm and an average width (measured in the direction parallel to the surface) of $\langle b \rangle = 20$ nm. Careful analysis of the SFM images and of the optical spectra obtained for different cluster sizes shows that the particle height is reproduced correctly; the width, however, is overestimated due to the finite radius of curvature of the SFM tip. The actual mean radius of the particles of $\langle r \rangle = 2$ nm was derived from the silver coverage and the cluster density as shown in the SFM images. In view of the aspherical shape of the particles the effective radius values refer to spheres with the same volume as the actual clusters

1.3 Determination of the shape of the particles

Because of the overestimation of the particle dimensions parallel to the surface by SFM, the shape cannot be deduced from the SFM images alone. In a recent publication, we have shown, however, that the axial ratio can be determined by combining SFM with measurements of the optical spectra of the clusters [13]. The spectra are dominated by plasmon polaritons, i.e. excitation of the free electrons driven by the electromagnetic field. The oblate clusters studied here exhibit two plasmon resonances, the (1,1) and the (1,0) modes, which are brought about by oscillations of the electrons in the direction of the long and short axis of the particles, respectively.

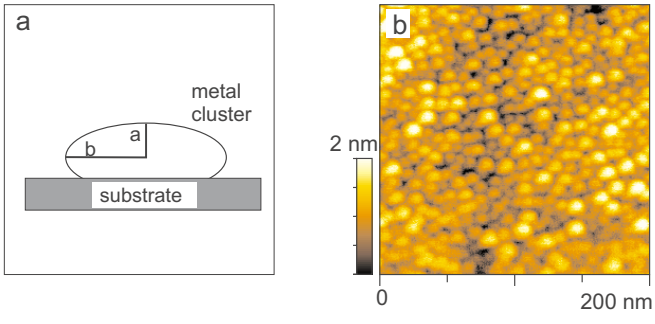

Fig. 1. a Schematic illustration and **b** Scanning Force Microscopy (SFM) image of the Ag particles on quartz substrates studied in the present paper. For details of the preparation conditions, see text

Their center frequencies are determined mainly by the shape of the aggregates, i.e. the axial ratio a/b. By comparison of the measured with the theoretical spectra calculated using electrodynamic theory, the mean shape of the experimentally prepared silver clusters was determined [13]. Examples of measured spectra are shown in Figure 2a. With increasing coverage, i.e. growing mean diameter, the (1,1) mode is red-shifted, whereas the (1,0) mode is blue-shifted. This indicates that the axial ratio a/b gradually decreases and the islands become more and more oblate as their mean size rises. The result of a quantitative analysis of the spectra is shown in Figure 3, where a/b is drawn by open squares connected by a dotted line to guide the eye. The axial ratio drops off from

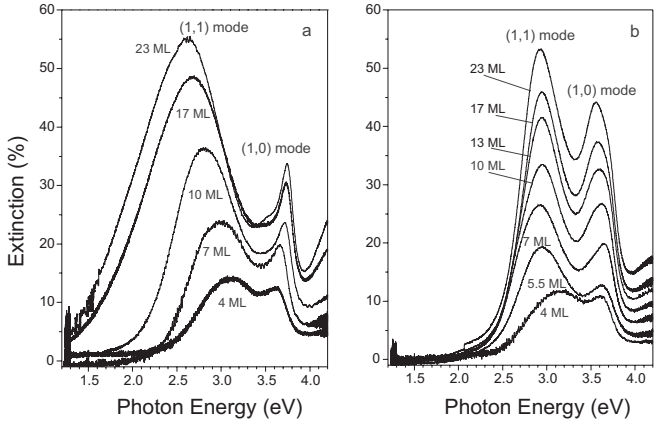

Fig. 2a,b. Optical extinction spectra of Ag particles on quartz substrates prepared by different Ag coverages given in equivalent monolayers (ML) **a** without and **b** with laser irradiation during growth. The laser wavelength and the fluence were set to $\lambda = 532$ nm and $\Phi = 400$ mJ/cm^2. The spectra were recorded for an angle of incidence of 45° with respect to the substrate surface normal by using p–polarized light of a Xe-arc lamp combined with a monochromator. The spectral resolution was 10 meV

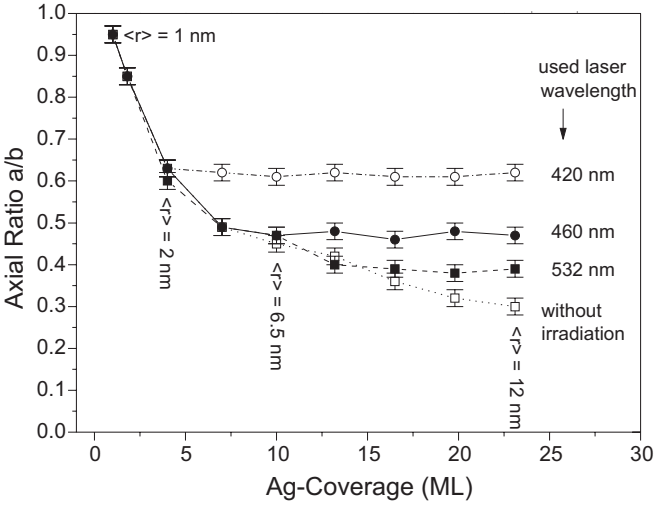

Fig. 3. Axial ratio a/b of oblate Ag particles deduced from their optical extinction spectra as a function of the Ag coverage for cluster growth without and with laser irradiation of different wavelength. For details of the determination of a/b see text and [13]. The fluence was kept constant at $\Phi = 50$ mJ/cm^2 for each wavelength. For particles made without laser irradiation the average radii $\langle r \rangle$ are also given. For coverages below 10 ML the different symbols used in the diagram, i.e. *full* and *open dots* and *squares*, are superimposed on each other

unity (very small, almost spherical clusters containing only about 15 atoms) to about 0.3 for clusters with $\langle r \rangle = 12$ nm, which corresponds to a coverage of 23 ML.

2 Method for nanoparticle shape control

In the following, the dependence of the position of the (1,1) plasmon mode on the axial ratio will be exploited to stabilize the shape of the clusters during growth by irradiating them with nanosecond laser pulses. The principle of the method is illustrated in Figure 4. As mentioned above, the undisturbed particles flatten with increasing size; see Fig. 4a,b. Simultaneously, the plasmon resonance shifts to lower photon energy. As a consequence, the photon energy $h\nu$ of the incident laser light can be chosen such that only clusters that have reached a certain axial ratio a/b absorb the light efficiently; see Fig. 4c,d. The deposited energy is rapidly converted into heat, and, provided the overlap between the slope of the absorption profile and the laser line is large enough to induce a sufficiently high temperature rise, evaporation of atoms is stimulated. Since these atoms are preferentially ejected from the edges and perimeters of the particles [16, 17], the axial ratio of the clusters grows. In short, a decrease in the axial ratio during deposition of atoms competes with the influence of laser irradiation, which increases the value of a/b. As a result, the shape of the generated clusters remains unchanged although the mean size grows.

The method introduced here to select and fabricate nanoclusters of a certain axial ratio is very simple to apply. In fact, it is even self-regulating in the sense that the slope of the absorption profile of the clusters automatically locks to the position of the laser line on the photon energy scale; see Fig. 4d.

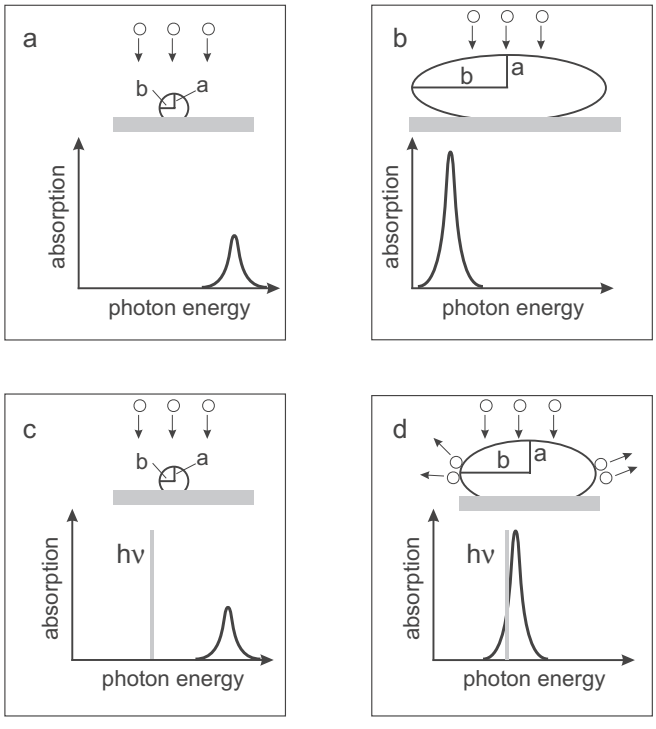

Fig. 4. Schematic illustration of the laser-based method for fabricating metal nanoparticles with well-defined shape, see text

This frequency constitutes a barrier that the nanoparticle excitation mode cannot pass. If the cluster absorption profile shifts towards the laser frequency during atom deposition, the absorption and therefore the evaporation rate grow and thus "repell" the profile from approaching further. Another advantage of the method is that the choice of the laser frequency automatically determines the axial ratio of the generated particles. Thus, nanoclusters of different, predetermined axial ratios can be made simply by using different wavelengths of the applied laser light (see below).

In addition to evaporation, laser-induced diffusion of atoms on the cluster surface might also contribute to the change of the shape of the particles during growth. Diffusion also tends to diminish the length of the large and increase that of the short axis [18, 19], the equilibrium shape of the particles being a truncated sphere with an axial ratio a/b close to unity [18, 19]. The relative importance of diffusion and evaporation cannot be determined unambiguously here. We would like to note, however, that our earlier related experiments [7] and calculations [20] on laser-induced narrowing of cluster size distributions by post-growth irradiation indicate that self-diffusion is negligible for nanosecond pulses.

At this point, it should be noted that laser-induced changes of the size and shape of small Ag and Au particles in aqueous solution and of Ag, Cu and Bi clusters in matrices have been reported [21–26]. In these studies, however, laser light was employed only after completion of cluster formation and no attempt was made to exploit different wavelengths for tailoring nanoparticles.

3 Demonstration of particle shape control

For laser treatment and shape stabilization during atom deposition the particles were irradiated with light pulses generated by a Nd:YAG laser or an optical parametric oscillator (OPO). The pulse duration was 7 ns and the repetition rate 10 Hz. Wavelengths of $\lambda = 420$, 460 and 532 nm were used and the fluence was set to values ranging from $\Phi =$ 50 to 400 mJ/cm^2. As explained above, the resonance positions of the two plasmon modes served as a measure of the shape of the nanoclusters.

Examples of extinction spectra of Ag clusters irradiated during growth with $\lambda = 532$ nm and $\Phi = 400$ mJ/cm^2 are shown in Fig. 2b. The flux of deposited Ag atoms was set to 1 ML per minute. As long as the mean particle size is $\langle r \rangle = 2$ nm, which corresponds to a coverage of 4 ML, there is no overlap between the laser line and the absorption profile. Therefore, at this stage, no influence of the light on the growth process is observed and the (1,1) and (1,0) modes are located at the same photon energies as those for clusters grown without laser irradiation. In contrast, the optical spectra of larger metal particles prepared under laser irradiation exhibit pronounced differences when compared to clusters made without using light: both modes remain fixed, whereas the amplitudes continue to increase; see Fig. 2b. Even if the integral coverage exceeds 20 ML, the positions of the plasmon resonances remain constant, the extinction growing to as much as 55%. We conclude from the experimental data that the method described above indeed stabilizes the shape of the nanoparticles efficiently and keeps the axial ratio constant. Its

value of $a/b = 0.50$ was derived by comparison of the experimental with theoretical spectra.

In order to further interpret and optimize the shape manipulation, the optical absorption coefficient of the silver particles was calculated as a function of their axial ratio for the applied laser wavelengths by using electrodynamic theory. The influence of the substrate and of electromagnetic coupling among the particles has been taken into account by a method published recently [13, 27]. The results of the calculations are shown in Fig. 5. The absorption coefficient follows the plasmon resonance and peaks at an axial ratio of $a/b = 0.28$ for $\lambda = 532$ nm. Therefore, *fully* resonant plasmon excitation with $\lambda = 532$ nm is possible in nanoparticles that have reached this shape during growth. The inset of Fig. 5 further shows that the absorption coefficient of the nanoparticles for this wavelength deviates noticeably from zero only for axial ratios below $a/b = 0.60$. This explains why the optical spectra of Fig. 2b are not affected by the light for coverages below 4 ML. Only for larger coverages does absorption occur and the competing interplay between deposition of atoms and removal by light commences. If $\Phi = 400\,\mathrm{mJ/cm^2}$ is chosen, like in Fig. 2b, the two counteracting processes can be balanced such that the two axes a and b grow by the same relative amount already for clusters with $a/b = 0.50$. If the fluence is smaller, clusters of constant shape are formed only if the axial ratio has dropped off to values below 0.50. This can be seen from Fig. 3b which displays experimental data collected with $\Phi = 50\,\mathrm{mJ/cm^2}$. With this fluence value and $\lambda = 532$ nm, clusters with a constant axial ratio of $a/b = 0.37$ are obtained as soon as the coverage exceeds about 12 ML. Naturally, the lower applied laser fluence must be compensated by the higher absorption coefficient of larger particles in order to induce the temperature rise needed for evaporation and diffusion.

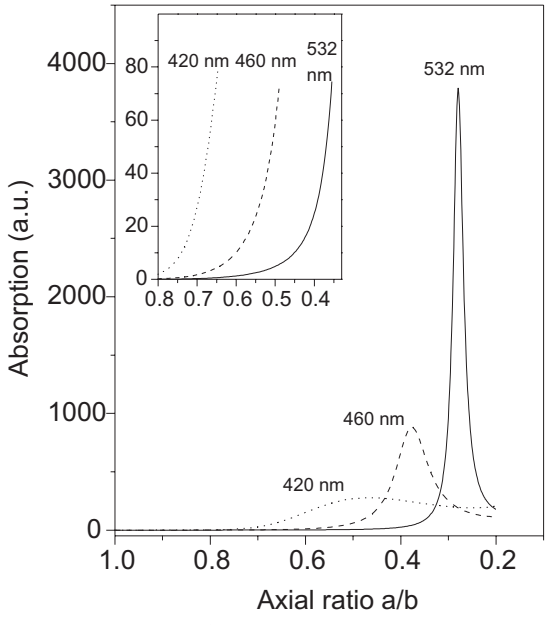

Fig. 5. Absorption coefficient of Ag particles on quartz as a function of their axial ratio calculated using electrodynamic theory for different wavelengths of the incident light. Details of the underlying theoretical model can be found in [7, 13, 20]. The *inset* shows an enlargement for axial ratios ranging from 0.8 to 0.33

An essential test for the versatility of the method is to vary the applied laser wavelength and examine its influence on the axial ratio of the grown nanoparticles. In fact, clusters with different a/b values were tailored simply by changing the wavelength. By applying $\lambda = 460$ and 420 nm, particles with $a/b = 0.47$ and 0.62, respectively, have been fabricated; see Fig. 3. This is possible since the maximum of the absorption curve shifts to larger axial ratios if the wavelength decreases; see Fig. 5. Because of this shift, laser manipulation commences at smaller coverages (smaller particle radii) if the wavelength is reduced. In Fig. 3 this is reflected in a deviation of the axial ratio at lower values as compared to undisturbed cluster growth. We finally mention that the optical spectra recorded with s-polarized light exhibit a single narrow resonance. As expected, it is located exactly at the same position as the (1,1) mode in Fig. 2b.

4 Conclusions

Our experiments have demonstrated the potential of the new technique to fabricate metal nanoparticles on substrate surfaces with predetermined, well-defined shape, i.e. axial ratio a/b. The method relies on the generation of particles through deposition of atoms and simultaneous irradiation of the substrate by nanosecond laser pulses. It is based on the pronounced shape dependence of the absorption coefficient of metal nanoparticles, in particular of the surface plasmon resonance, and can be applied to a wide range of cluster sizes as long as the shift of the plasmon frequency as a function of a/b predominates its variation on the cluster diameter. This condition is fulfilled for mean radii below about 50 nm. Moreover, the method demonstrated experimentally here for Ag particles on quartz substrates should be applicable at least to all those nanoparticles that exhibit sharp plasmon resonances like, for example, Au, Cu, Al, Ta and alkali metal clusters.

The ability to fabricate metal nanoparticles of desired shape almost irrespective of their sizes opens up the possibility to examine the dependence of the chemical and physical properties of these systems with reduced dimensions on their shape in future experiments. In addition, the particles can be easily covered with a protective layer, or embedded in matrices to exploit them in technological applications including, for example, linear and nonlinear optical devices. Along these lines, it will be of particular importance and value that the position of maximum extinction on the wavelength scale and its magnitude can be chosen independent of each other.

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References

1. P. Jena, S.N. Khanna, B.K. Rao (Eds.): *Proceedings of the Science and Technology of Atomically Enginieered Materials* (World Scientific, Singapore 1995)
2. H.H Anderson (Ed.): *Small Particles and Inorganic Clusters*, ISSPIC 8 (Springer, Berlin, Heidelberg 1997)
3. G. Timp (Ed.): *Nanotechnology* (Springer, New York 1999)
4. R.F. Haglund, Jr.: In *Optics of Small Particles, Interfaces and Surfaces*, ed. by E. Hummel, P. Wißmuth (CRC Press, Boca Raton 1996)

5. M. Valden, X. Lai, D.W. Goodman: Science **281**, 1647 (1998)
6. M. Haruta: Catal. Today **36**, 153 (1997)
7. J. Bosbach, D. Martin, F. Stietz, T. Wenzel, F. Träger: Appl. Phys. Lett. **74**, 2605 (1999)
8. H. Brune: Surf. Sci. Rep. **31**, 121 (1998)
9. C.R. Henry: Surf. Sci. Rep. **31**, 231 (1998)
10. M. Bäumer, J. Libuda, A. Sandell, H.-J. Freund, G. Graw, Th. Bertrams, H. Neddermayer: Ber. Bunsenges. Phys. Chem. **99**, 1381 (1995)
11. B. Müller, L. Nedelmann, B. Fischer, H. Brune, K. Kern: Phys. Rev. B **54**, 17 858 (1996)
12. H. Brune, M. Giovanni, K. Bromann, K. Kern: Nature, **451** (1998)
13. T. Wenzel, J. Bosbach, F. Stietz, F. Träger: Surf. Sci. **432**, 257 (1999)
14. F. Balzer, S.D. Jett, H.-G. Rubahn: Chem. Phys. Lett. **297**, 273 (1998)
15. M. Vollmer, U. Kreibig: *Optical Properties of Metal Clusters*, Springer Series in Mater. Sci., Vol. 25 (Springer, Berlin, Heidelberg 1995)
16. M. Vollmer, F. Träger: Surf. Sci. **187**, 445 (1997)
17. C. Xu, W.S. Oh, G. Liu, D.Y. Kim, D.W. Goodman: J. Vac. Sci. Technol. A **15**, 1261 (1997)
18. M. Drechsler: On the Equilibrium Shape of Metal Crystals, in *Surface Mobilities on Solid Materials, Fundamental Concepts and Applications*, ed. by Vu Thien Binh, Nato ASI Ser. B 86 (Plenum Press, New York 1983)
19. R. Kern: In *Morphology of Crystals*, ed. by I. Sunagawa (Terra Scientific, Tokyo 1987)
20. J. Bosbach, T. Wenzel, F. Stietz: unpublished
21. K. Kurita, A. Takami, S. Koda: Appl. Phys. Lett. **72**, 789 (1997)
22. S. Park, T. Isobe, M. Senna, R. Weeks, R. Zuhr: Appl. Phys. Lett. **73**, 2687 (1998)
23. F. Gonella, G. Mattei, P. Mazzoldi, E. Cattaruzza, G.W. Arnold, G. Battaglin, P. Calvelli, R. Polloni, R. Bertoncello, R.F. Haglund, Jr.: Appl. Phys. Lett. **69**, 3101 (1996)
24. A.L. Stepanov, D.E. Hole, P.D. Townsend: Nucl. Instrum. Methods B **149**, 89 (1999)
25. A.L. Stepanov, D.E. Hole, A.A. Bukharaev, P.D. Townsend, N.I. Nurgazizov: Appl. Surf. Sci. **136**, 298 (1998)
26. R.A. Wood, P.D. Townsend, N.D. Skelland, D.E. Hole, J. Barton, C.N. Afonso: Appl. Phys. Lett. **74**, 5754 (1993)
27. T. Yamaguchi, S. Yoshida, A. Kinbara: Thin Solid Films **21**, 173 (1974)