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SILVER QUANTUM DOTS DEPOSITED ON YAG COATED SILICON WAFER

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Abstract. Silver nano-dots have been deposited by a special procedure on the surface of a YAG coated silicon wafer. Sizes of 40–100 nm and a self-organized distribution according to the pattern of the pattern of defects (dislocations, terraces, etc.) on the wafer's surface were revealed. The procedure is simple and can be applied for the controlled deposition of small silver clusters to be used both in medicine and in nano-electronic devices.

Key words: silicon wafer, Nd:YAG-laser, silver quantum dots, YAG coating.

1. INTRODUCTION

The academician I. I. Popescu was the first who evidenced the formation of icosahedral and dodecahedral ordered clusters of argon in gas phase in his pioneering work with von der Heide [1]. A time-of-flight technique was used for the measurement of positive ion mobilities in argon in the 1–100 atm pressure range at 300°K. The ions were produced by photo-ionization of gas atoms in the drift region with ultraviolet light from a spark discharge. A mobility was found which varies continuously with the reduced electric field E/p_0 and which exhibits two saturation values at 1.55 ± 0.01 cm^2/V·s (for $E/p_0 \sim 2$ V/cm Torr) and at 0.818 ± 0.003 (for $E/p_0 \sim 0.17$). The former value proved to be in excellent agreement with the zero-field mobility obtained for Ar^+. The last value was interpreted in terms of the Langevin theory and connected with the formation of the Ar_{33}^+ labile cluster. This has the Ar^+ ion as nucleus and is surrounded by two complete shells of 12 and 20 Argon atoms, respectively. A mean value of the cluster radius has been estimated as 6.24 Å.

Many years after this paper was published, the field of nano-clustering and self organization in inorganic phases developed tremendeously with the aim to understand the ordering in the solid matter and for preparing the future applications in nanotechnologies including nanoelectronics, spintronics or quantum computers.

For the last decade we became the witnesses of massive astonished advance in the field of nanoscience and nano-manipulations [2–5]. However, it is not always and everywhere supported by a true realization of an ambitiously declared bottom-up approach to the molecular technology. With creating new systems and devices the understanding of origin of considerable technological difficulties with which the researchers of modern technologies collided during some previous years has become much clearer. The self-organization of one or more entities occurs when the total energy of the system is minimized to result in a more stable state. The process of self-assembly inherently implies: 1. some mechanism where movement of entities takes place using diffusion, electrical fields, etc. 2. the concept of "recognition" between different elements that results in self-assembly 3. where the "recognition" leads to the binding of the elements dictated by forces (electrical, covalent, ionic hydrogen bonding, van der Waals, etc.) such that the resulting physical placement of the entities pushes the system in the state of lowest energy.

Self-assembled processes could have a variety of applications. They are important in any case where micro- or nanoscale objects of one type need to be placed or assembled at specific sites on other substrate. Applications could include: a) detection and diagnostic of radiation, b) fabrication of novel electronic/optoelectronic systems, and c) new material synthesis.

In recent years a high interest raised in the developing concepts and approaches for self-assembled systems for electronic and optical applications. Material self-assembly has been demonstrated in a variety of semiconductors (GaAs, InSb, SiGe…) using Stransky-Kastranov strain-dependent growth of lattice mismatch epitaxial films. There is a continuous interest in assembling semiconductor transistors [6], carbon nanotubes [7, 8] and quantum wires [9, 10], which can be used as active devices for memory and logic applications. The self-organization in amorphous materials seems to be of potential interest for three-dimensional integration of nano-scale devices.

Recently, Lucovsky [11] has reported self-organizations that prevent percolation of network and interfacial bond-strain, which lead to intermediate phases (Boolchand phases) with low concentration of defects in systems as: Si_3N_4:H, SiO_2 interfaces, Ge-Sb-Te chalcogenide films, etc. Self organization is accompanied by the observation of non-statistical bonding arrangements, the number of bond-stretching and bond-bending constraints/atom being fluctuating.

Specific islands were epitaxially grown on GaAs substrate [12]. The authors concluded that InAs islands randomly nucleate; it is a random distribution of $In_xGa_{1-x}As$ ring-shaped islands. A 2D lattice of InAs islands on a GaAs substrate was formed.

After decades of work, the growth of continuous thin films, *i.e.*, two-dimensional structures, is progressively becoming a technological issue more than a field of fundamental research. Incidentally self-organization of nanostructures on surfaces is now an important field of research, *i.e.*, structures of low dimensionality (two, one or zero), attracted attention in the past five years with a steep rise. Whereas self-organization was initially motivated by potential applications, it has up to now essentially contributed to the advancement of fundamental science in low dimensions, as model systems could be produced that could not have been fabricated by lithography [13].

Self-organized Ag nanodots were deposited by Kinoui Matchi and co-workers on Si(100) by a pulsed laser deposition method. A compact apparatus was specially developed for this purpose with Nd:YAG-laser. Factors dominating size and morphology of the nanodots were examined by systematically varying species and pressure of the gas in the deposition chamber, deposition time, and the target-substrate distance (TSD). It is particularly to be noted that decreasing TSD from 100 mm to 50 mm brought about an increase in the dot size from 5 ± 2.1 nm to 9 ± 3.3 nm at Ar pressure, 100 Pa, and deposition time, 3min. The factors making self-organized Ag nanodots were discussed, and key values were proposed to evaluate the assembly of dots.

Scanning tunneling and Auger spectroscopy were used to study the formation of silver nanostructures at room temperature on a Si(557) surface containing regular atomic steps with a height of three interplanar spacings. The shape of silver islands formed on the surface was found to be affected by oxygen adsorbed on the silicon surface from the residual atmosphere in a vacuum chamber. Depending on the amount of adsorbed oxygen, silver nanostructures can be obtained in the form of nanowires extended along the edges of steps or nanodots ordered as lines parallel to these edges.

Because of their novel electronic and optical properties, many technological applications have been proposed for quantum dots. A key requirement for these applications is the ability to predict and control the geometry and material properties of both single dots and arrays of dots. The kinetics pathways to formation and organization of quantum dots are important because the spacing and regularity of a quantum-dot array is largely determined at the early stages of their growth. The most common growth mode for quantum dots is Stranski-Krastanov (SK), in which growth of a wetting layer precedes the three-dimensional islanding that leads to quantum dots. Computations of epitaxial growth have been surprisingly unsuccessful in simulating SK growth, and the reasons for this failure are not well understood. Strain due to lattice mismatch between the substrate and film is an essential ingredient in SK growth and self-assembly of quantum dots. Inclusion of strain in models for material growth and device properties has proved to be difficult and computationally complex due to the short times scales of atomistic processes and the long-range influence of strain.

In this paper we report a new procedure for silver nanodot deposition based on evaporation-deposition competitive processes stimulated by a high temperature treatment of the YAG coated silicon wafers provided on the back side with silver paste.

2. PREPARATION OF THE SUBSTRATE

YAG is an important material for laser production and is applied in crystalline form, doped by Neodymium. The amorphous phase of YAG has been not prepared nor understood up to day. Thin YAG films were deposited on silicon (100) wafer by pulsed laser deposition (PLD) using a KrF*excimer laser (248 nm wavelength of the emitted UV pulse, pulse duration < 10 ns, 1Hz repetition rate, and maximum output energy of 85 mJ/pulse). The pulse was focused on the target through an MgF_2 cylindrical lens (focal length: 30 cm) argon coated. The incidence angle to the target was 45°. The laser spot was set within 4.2 and 6.4 mm^2 and the incident fluency varied roughly in the range 0.8–1.6 J/cm^2. The target material were platelets of $15 \times 15 \times 2$ mm^3 cut from bulk YAG crystal grown by Czochralski method using high purity elements. The target holder was placed in a stainless vacuum chamber, which was subsequently evacuated down to $1–7 \times 10^{-4}$ Pa. The target was rotated with the frequency of 0.4 rot/min during PLD process. The substrate for film deposition was a [100] oriented silicon wafer mounted on a molybdenum heating block, parallel to the target surface and placed at a distance of 2–5 cm. The number of pulses applied for making one film was 30 000. The deposition was made in three successive stages.

From the ellipsometric measurements we have found a thickness of 1.9 μm for the fresh film. This means a deposition rate of 0.63 Å/ pulse. A refractive index of 1.84 at 700 nm was determined. The structure of the films has been determined by X ray diffraction and scanning electron microscopy. A TUR M62 diffractometer provided with copper target tube was used. An Amray 1830 I scanning microscope was used for the microscopy studies.

3. XRD RESULTS

The as-prepared film was investigated firstly by X-ray diffraction. The fresh film of YAG is amorphous (Fig. 1). An intense first maximum and a large, weak second maximum are the most important characteristics of its X-ray pattern.

The X-ray diagram of YAG powder and YAG thin film deposited by PLD and annealed 1 h at 1100°C are shown in Fig. 2. The annealed film is crystalline. High temperature treatment of YAG film induced the formation of crystalline phase of

YAG, somewhat depleted in Yttrium. The sub-stoichiometry of YAG film was proved by the lattice parameter "a", of the YAG phase. In the stoichiometric phase $a = 12.016$ Å, while in the sub-stoichiometric phase (our film) $a = 12.253$ Å (calculated from the peak positions). A minute amount of crystalline yttrium oxide was detected in the film.

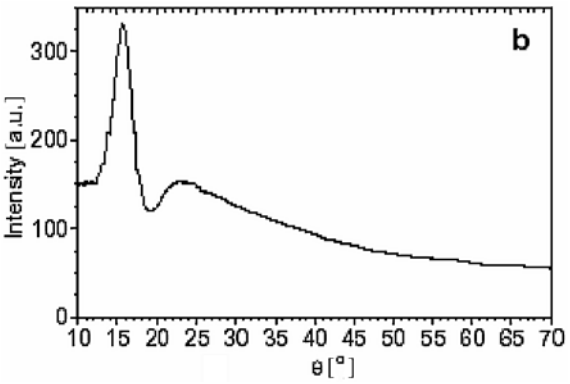


Fig. 1 – The X-ray diffraction diagram of YAG film on silicon wafer prepared by PLD.

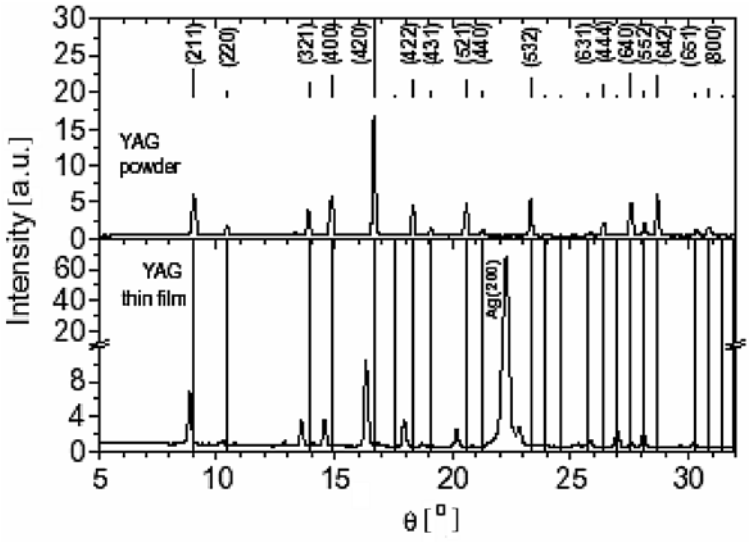
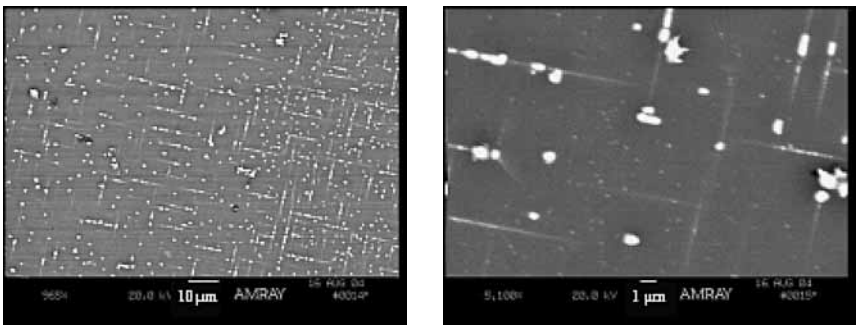


Fig. 2 – The X-ray diffraction diagram of YAG film on silicon wafer prepared by PLD and annealed 1h at 1100°C.

4. SILVER QUANTUM DOT DEPOSITION

In order to prepare nanodots, the silicon wafer was covered by silver paste on the back-side of the silicon plate coated by YAG amorphous film. The system was

put in a closed furnace and annealed at 1100°C for one hour. After annealing the furnace was cooled down to room temperature. Finally, the wafer was taken off the furnace and was investigated by X-ray diffraction and scanning microscopy. The structural results are presented in Fig. 2 and the microscopy results are shown in Fig. 3. In Fig. 2 the X-ray narrow lines indicate the formation of large YAG crystallites. Moreover, a peak ascribed to crystalline silver is clearly observed. The peak is wide, compared with the peaks of YAG and this witnesses that Ag crystallites have nanometric size.



a b

Fig. 3 – Silver nanodots on the surface of langasite coated silicon.

The explanation of the presence of Ag on the diagram is as follows: the heat treatment at high temperature determine the evaporation of the silver from the back side of the wafer and re-deposition on the surface of the plate. Both processes of evaporation-condensation taking place dynamically lead to the self-organization of silver as small clusters or nanodots. The nanodots are deposited on the dislocation pattern or step defects of the YAG crystalline coating, that takes the orientation of the silicon wafer (Fig. 3a). Thus a regular distribution along several parallel lines can be observed. The dots look in the image as round disks. The average size is situated around 400 nm. As can be observed on Fig. 3b three types of silver nanodots were formed. The dots of smallest size consists of randomly deposited round dots of ~100 nm in diameter. The density of these dots is 10^7 dots/cm^2. Other group of dots of lower surface density (10^6 dots/cm^2) are characterized by larger diameters (~1000 nm). Several dots are oblong with the length of 1.5 μm and thickness of 0.5 μm.

5. DISCUSSION

Self-organization and spontaneous ordering into the periodic structure can be found in different fields of science. This phenomenon, known as the spontaneous

pattern formation, arises from the interplay between the self-action (non-linearity) and long-range interaction between particles. When these tendencies act in an opposite fashion on the local perturbation, they result in the breakup of a homogeneous state, initiated by small random fluctuation ("noise"); perturbations with a particular periodicity are enhanced, forming regular patterns, such as stripes or hexagons.

It was shown that the irradiation with a single uniform coherent polarized laser beam at normal incidence onto pDR1M polymer thin film resulted in the spontaneous patterning of submicrometer hexagonal structures at the polymer surface (Fig. 4).

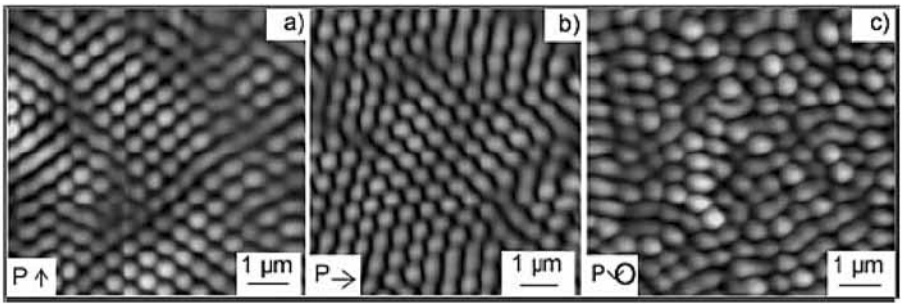


Fig. 4 – AFM images (7×7 μm^2) of hexagonal structures on the pDR1M polymer film for: a) vertically, b) horizontally, and c) circularly polarized incident laser beam (300 mW·cm^{-2}, 514 nm. Thickness of the sample were 220 (a) and 350 nm (b, c), exposure times were 100 (a) and 80 min (b,c).

Semiconductor nanostructures have attracted tremendous interest in the past few years because of their special physical properties and their potential for applications in micro- and optoelectronic devices. In such nanostructures, the free carriers are confined to a small region of space by potential barriers, and if the size of this region is less than the electron wavelength, the electronic states become quantized at discrete energy levels. The ultimate limit of low dimensional structures is the quantum dot, in which the carriers are confined in all three directions. Therefore, a quantum dot can be thought of as an artificial atom. The fabrication of quantum dots presents a formidable challenge because the small dimensions required for quantum dots are at the limit of lithographic and semiconductor processing techniques and also because the dot interfaces must be kept defect-free in order to obtain the high-quality electronic properties that are required for device applications. As a consequence, many efforts have been made to develop alternative routes for the fabrication of quantum dots that are based on the principle of self-organization.

The spontaneous formation of three-dimensional (3D) islands in strained-layer hetero-epitaxy has recently emerged as a new technique for the synthesis of

self-assembled quantum dots. This technique is based on the fundamental morphological instability of strained surfaces, which is driven by the elastic relaxation of strain energy in the freestanding islands that spontaneously nucleate on the surface of a growing epitaxial layer after the completion of the wetting layer. In the early stage of growth, these islands are defect-free and fully coherent to the substrate. Therefore, quantum dots are obtained in situ without the interface problems that are associated with *ex situ* processing techniques. However, although single quantum dots exhibit extremely sharp, atomic-like luminescence properties, the considerable inhomogenous line broadening in larger dot ensembles due to nonuniformities in the dot sizes has posed considerable limitations for device applications. Springholz *et al.* [14] studied the idea that the vertical elastic interaction of the strained 3D islands during the epitaxial growth of quantum-dot superlattices can lead to a lateral ordering and size homogenization of the dots. Molecular beam epitaxy was used to fabricate PbSe quantum-dot superlattices, in which each dot layer is separated vertically by $Pb_{1-x}Eu_xTe$ spacer layers. For our materials, the ordering mechanism is so efficient that a nearly perfect hexagonal two-dimensional (2D) dot lattice was obtained within the growth plane after a few superlattice periods. Detailed high-resolution X-ray diffraction investigations revealed the existence of a dot correlation that is not parallel but is along crystallographical directions inclined by 39° to the growth direction. As a result, 3D quantum-dot crystals were formed with a fcc-like A-B-C-A-B-C stacking sequence. Theoretical calculations of the elastic interaction between the buried dots clearly showed that this special correlation, as well as the efficient lateral ordering, was directly connected to the high elastic anisotropy of the semiconductor compounds consisting of the group IV and VI elements of the periodic table (lead salt compounds). Because the symmetry of the dot arrangement is fixed by the elastic anisotropy, the lattice constant of the dot crystals can be tuned continuously over a range of several tens of nanometers just by changing the spacer layer thicknesses. This effect provides an opportunity for the tuning of optical and electronic properties. The self-organization of pyramidal PbSe islands that spontaneously form during strained-layer epitaxial growth of $PbSe/Pb_{1-x}Eu_xTe$ ($x = 0.05$ to 0.1) superlattices results in the formation of three-dimensional quantum-dot crystals. In these crystals, the dots are arranged in a trigonal lattice with a face-centered cubic (fcc)-like A-B-C-A-B-C vertical stacking sequence. The lattice constant of the dot crystal can be tuned continuously by changing the superlattice period. As shown by theoretical calculations, the elastic anisotropy in these artificial dot crystals acts in a manner similar to that of the directed chemical bonds of crystalline solids. The narrow size distribution and excellent control of the dot arrangement may be advantageous for optoelectronic device applications. The long-range elastic interaction is emphasized to be the common driving force for the formation of both equilibrium structures and kinetically controlled structures (Fig. 5).

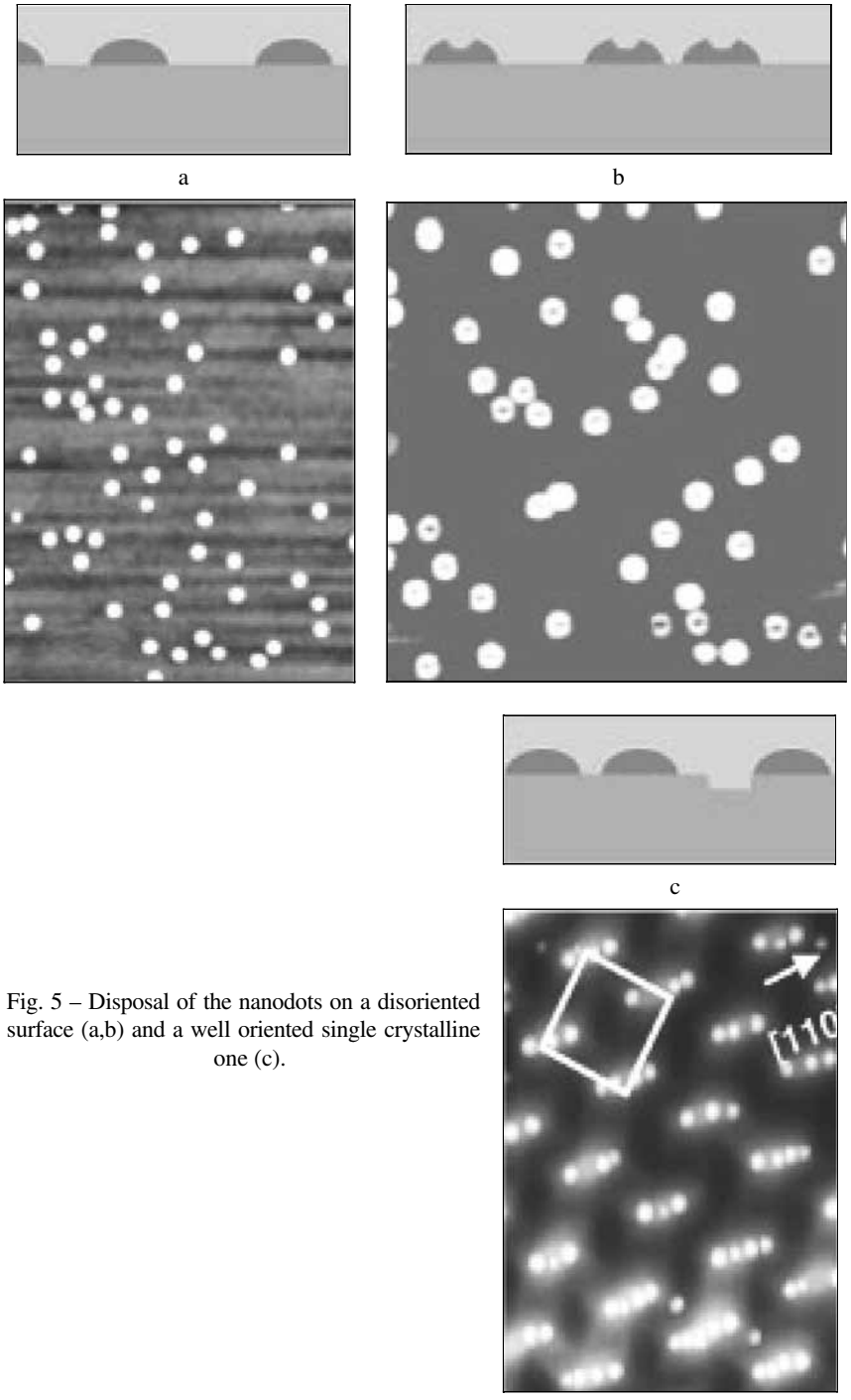


Fig. 5 – Disposal of the nanodots on a disoriented surface (a,b) and a well oriented single crystalline one (c).

Similar effects are responsible for self-organization of periodically corrugated surface structures and ordered dot arrays on crystal surfaces. Strain relaxation on facet edges may result in the appearance of periodically corrugated surfaces for lattice-matched growth. Strain relaxation on facet edges and island interaction via the strained substrate act as driving forces for the formation of ordered arrays of uniform, strained lattice-mismatched islands on a crystal surface. A pseudo-periodic square lattice is manifested for the InAs-GaAs(100) system. Less ordered dots are formed on the GaAs(100) surface with a 4 monolayer GaSb deposition. New experimental methods are applied for the characterization of faceted nanoscale structures. For GaAs-AlAs multilayer structures grown on (311)A substrates, interface corrugation results in optical anisotropy of the same sign as expected from the low symmetry growth direction, making the main origin of the anisotropy unclear. The quantitative optical reflectance and reflectance anisotropy studies show that the interface corrugation plays an important role for thin (less than 4 nm) GaAs layers. MESA arrays from samples with InAs quantum dots grown on (100) surface are fabricated. The photo-luminescence intensity is found to depend only weakly on the MESA size (1000 nm to 250 nm).

If we compare the distribution of silver nanodots on the surface of the silicon wafer coated by thin crystalline YAG epitaxially oriented layer, with a classical image of dot distribution on (110) oriented surface, the conclusion is that the disposal of the dots is along the main crystalline axis as short or longer rows of points well aligned.

6. CONCLUSIONS

New procedure for nanodot preparation was developed and applied to silver material. The procedure can be used for getting ordered silver nanodot arrays by self-organization if appropriate patterning of the silicon (or other crystal) is ensured on the deposition surface.

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