Nanotechnologies in Printing and Packaging

(Some educational, scientific and technological problems of nanosized systems preparation and applications in printing and packaging)

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There are considered the trends in microminiaturization in printing and some features of dispersed systems in nano sized scale as well as their applications in Graphic Arts and packaging. Nanoparticles, nanostructures, nanocomposites are regarded as dispersed formations with unique properties due to quantum-sized and surface effects. The photolithography and modern imprinting lithography methods are shortly made out for what the short history of Graphic Arts development and printing of packaging is overviewed as for applications of dispersed materials. There are concerned the dispersed particles in photosensitive layers which were widely applied in Graphic Arts and printing electronics. The modern imprinting lithography as a kind of nanotechnology is concerned in view of future security printing, producing RFID tags and other applications for packaging. There is made an analysis of the modern state of nanotechnology using in materials and processes for packaging and printing concerning the developments of new kinds of graphic communications.

Introduction

The achievements and perspectives of nanosciences and nanotechnology determine the modern stage of scientific and technical progress. Printing and packaging are now and will be influenced by the achievements. Thus as example, electronics industry is seeking next generation manufacturing methods to produce cheaper, smaller, and more flexible components. The trend toward ever-smaller semiconductors was first noticed as long ago as 1965. That's when Gordon Moore foresaw the future state and formulated what is now known as Moore's Law: The number of components that can fit on an integrated circuit (and quantity of information, correspondently) doubles every 18 months to two years [1]. On the Moore's diagram at beginning of 1980-es the minimum dimension of elements of electronic devices to the period of 2005-2010 must be less 0.1 μm or 100 nm [2]. It means that elements in electronic devices must have sizes of nanometer dimension.

The imprinting lithography is now one of the perspective ways for producing micro- and nanosized devices. That is why it is reasonable to look at the lithography and photolithography history at all, as well as the way of their transformation to one of the progressive manner for miniaturization, and to show some principles and historical aspects of dispersed systems using in Graphic Arts and photographical methods including educational, scientific and technological problems of nanosized systems preparation and applications in printing and packaging.

Why nanosystems are of interest and importance?

Now the words like nanotechnology, nanophysics, nanochemistry, nanocomposites became rather popular and very important. Fundamental scientific investigations are obtaining essential support from leading industry firms and state organisations. Nonosciences and nanotechnologies are now in the first line of scientific and technical progress. The winners of Nobel prizes for 2007 year in physics (A. Fert and P.Gruenberg) and chemistry (G.Ertl) were awarded for scientific achievements and practical applications in field of nanophysics and nanochemistry. There is organised from 2008 the special so called "Parallel Nobel Prize" in area of nonothechnologies with equal to the Nobel prizes financial level.

What does "nano" mean indeed? The Greek word "nanos" means a draft that is very small man or woman. We know a scale of length: meter (m), millimeter (mm) = 10 $^{-3}$m, micrometer (μcm) = 10 $^{-6}$m, nanometer (nm) = 10 $^{-9}$m. Thus particles which have size of several nanometers –a few tens of nanometers, some time a hundred nanometers are called as nanosized particles or nanoparticles, nanocomposites, nanostructures, nanofibres, nanotubes.

Now is well known that nanoparticles can have quite unusual physical and chemical properties. That opens new ways for creation and development of new substances, materials and processes. That's why the attention and interest to this field of science and technology were growth extraordinary the entire world. There are editing new magazines dealt with only these topics. The results of researches in these areas of science are among the most important publications in well known "old" magazines such as for example "Journal of American Chemical. Society". Printing and packaging cannot be a side from the trends of scientific and technical development.

Nanosized particles are dispersed systems that traditionally had been the object of colloid chemistry which is indeed physics and chemistry of dispersed systems of the wide dimension and surroundings range. Now the interest of researchers to nanosized systems excites by the fact of inconvenient properties due to quantum-sized effects. One of the main reasons of the changes at the transfer to nanoscale sizes is the enlarging of part of surface atoms in dispersed phase if compare to the volume phase. Decreasing of sizes of dispersed particles leads to the essential growth of surface energy including free surface energy and chemical potential. Some displays of that are changes in optical spectra. Absorbance of nanosized dispersions shifts to short waves. The aggregation of nanoparticles leads to shift into long wave's area (Fig. 1).

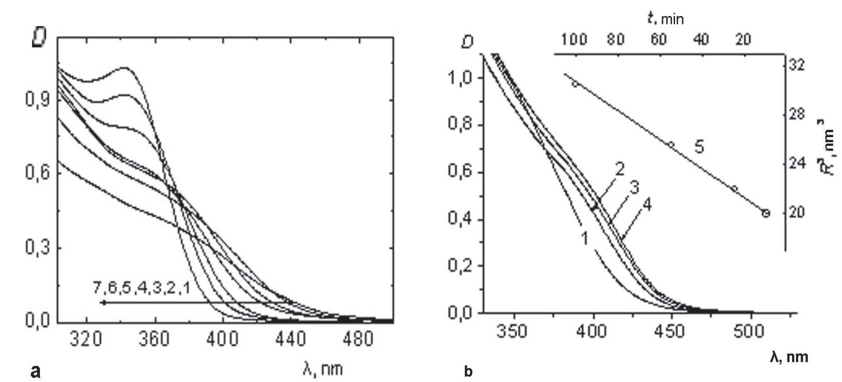

Figure 1: Absorption spectra of colloid solutions of $Cd_xZn_{1-x}S$ at the Na_2S abundance, x=0.5.

(a) The concentrations of Na_2S surplus were 0 (1), $1 \cdot 10^{-4}$ (2), $3 \cdot 10^{-4}$ (3), $5 \cdot 10^{-4}$ (4), $1 \cdot 10^{-3}$ (5), $1.5 \cdot 10^{-3}$ (6) and $5 \cdot 10^{-3}$ M (7).

(b) The spectrum of the fresh prepared colloid solution (1) and spectra of the self-restrained solution at 95-98 ^{0}C during 25 (2), 55 (3) and 100 minutes (4). The line 5 is a dependence of nanoparticles sizes from time of their preparing.

We can say that nanosized particles were probably to be present in many dispersed colloid solutions and polymer layers at all. That is applicable for example to light sensitive thin grain argentums halogenid emulsions. But there could not be displayed their interesting properties in wide range of dispersions. From these positions we can look at many dispersed systems which had been applied in historical development of Graphic Arts.

Lithography and other kinds of printing

We can say that the principal materials in Graphic Arts production (papers, printing inks, polymer films, photographical layers) are dispersed systems indeed (Fig. 2).

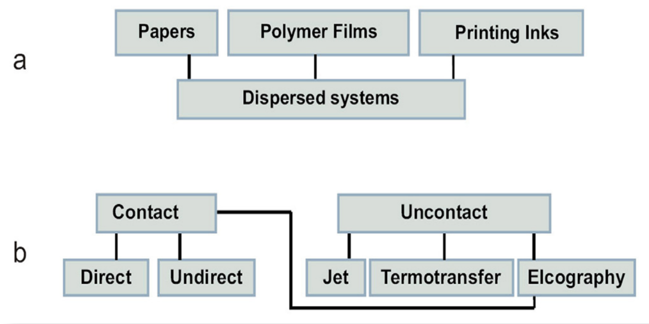

Figure 2: Principal materials (a) and processes (b) in Graphic Arts Production

Printing processes consist in mass transfer to printing plate and then from the printing plate to printed material – paper, plastics, metal. The printed material surface is usually a dispersed system. And the transferred substances – printing inks or varnishes are dispersed materials too. The printing process can occur through contact (common printing processes) or without contact with printing elements of printing plate. The last case may be realized in jet, thermo (as well as electro-) transfer or elcography, which means electro condensational printing.
There are need to say a few words about the history of printing. It's now well known that classic printing processes were initiated in China and Korea at finish of the first Millennium after Christ [3]. The materials for letterpress printing plates preparing were at first wood and clay (ceramics) and than metal alloys. In all the cases the surface of typing elements of the plates was rather large. And these elements –separate letters were raised over the level of imprinting areas. That is letterpress printing (high print, in German -"Hoch Druck"). Nowadays this kind of printing is represented by flexography. Gravure represents another kind of printing when typing elements are deepened. The important principle step in printing technology was made by invention (A. Senefelder, 1798) planar lithographic printing. The difference in surface properties of typing and untyping elements of the stone plate was the main principal feature for lithography; collotype and later till classic and waterless offset printing nowadays (Fig. 3).

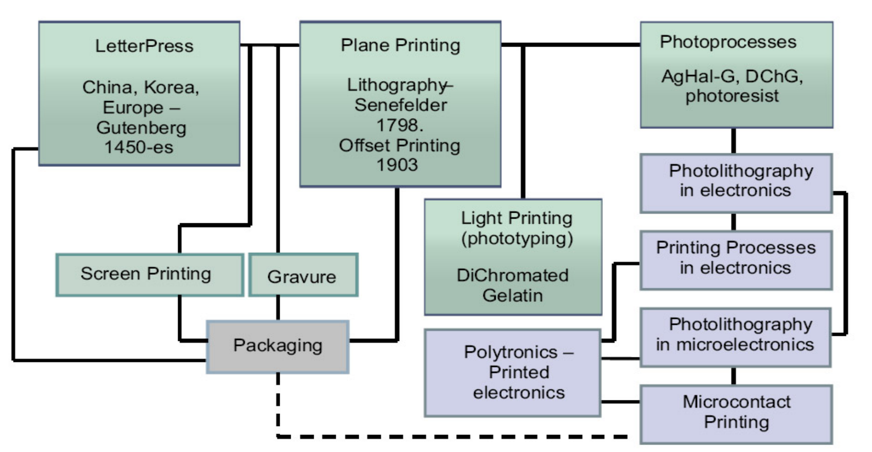

Figure 3: Development stages of Printing and its application.

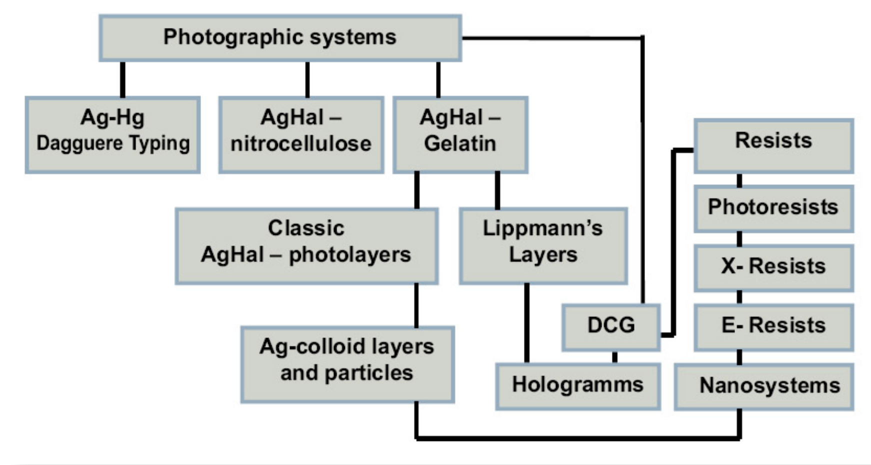

Figure 4: Photographic (dispersed) Systems in Image Formation

Photographic Systems in Image Formation

The principle changes occurred in Graphic Arts from the middle of the XIX century due to invention of photographic processes for the information registration. Discovery and invention of photography occurred in the first half of the XIX-th century. «Three persons may be accounted as the first inventors of photography. They are Niciphor Nieps (1765-1833), Jack Dagguere (1787-1851), Fox Talbot (1800-1877). The first created heliography, which was a base for photochemical techniques in Graphic Arts. The second started the real photographic process. The third carried out the principals of negative-positive process… All the processes were developed without a sufficient scientific ground». (K. V. Chibisov, 1986). Due to the last thesis there were attempted and studied a grate number of organic and inorganic systems before the grounds of photographic science were formulated.

Graphic Artists were among the first who used the invention of photo registration to make illustrative printing plates. That was nitrocellulose and then gelatine layers which contained light sensitive argentums halogenid dispersions. The very important consecutive step was invention of light sensitive material dichromated gelatin - layers of water soluble denatured protein collagen with dichromate – the salts of chromic acid (Talbot, 1840) [4]. This material had been used practically in all classic kinds of printing known – letterpress, gravure, collotype, offset, and silk-screen printing. And now it is used widely in holography. It was accounted as largely transparent homogeneous not dispersed material. But it is not so in light exposed layers. Some steps of using photographic systems in the printing development and other applications are seen in Fig. 4.

Thus, practically all important photographic layers are the dispersed systems. That limited the resolution of the registering media and registrant images. For printing technologies it was not very important. But for electronics where the high resolution ability of copying layers or photo resists, is a very necessary feature. We may remain that progress in electronics starting from the invention of transistors was connected with some printing technology principles applications. They were printed circuits and now are printed electronics as well as photo resists in photo microlithography.

Photolithography nowadays

The trend toward ever-smaller devices was first noticed as long ago as 1965 and later when the Moore's law showed to be fulfilled. .

The number of components that can fit on an integrated circuit doubles every 18 months to two years [2, 3]. That was a time when the ground technological method in circuit production was micro photolithography. In general a term that is the process used to create micrometer or sub micrometer scale structures for fabricating various kinds of devices, including integrated circuits, biochips, optical components.

Since the 1960s, microlithography has been dominated by the use of light and photosensitive material to etch details onto a silicon substrate. In a sense, this photolithography can be thought as a high-end projection camera that can cast the details of a circuit layer from a photo mask to a photosensitive material on the wafer. While it can take a few hours to inscribe the photo mask using a slow, serial process, photolithography allows for the nearly instantaneous parallel transfer of millions of pixels of data from the photo mask to the wafer.

The use of progressively shorter-exposure wavelengths, along with an increased complexity in photo mask design, has led to the reduction of the minimum feature size in photolithography. Leading-edge photolithography now operates at a wavelength of 193 nanometers. There are can be etched pattern structures at this wavelength with a half-pitch as low as 90 nm. The continuous reduction in wavelength—researchers are now investigating extreme short waves illumination at 13.2 nm—combined with highly sophisticated designs of lenses, mirrors, and masks, and with innovation in materials, processes, and machines will probably enable sub-70 nm photolithography, and may even enable sub-50 nm photolithography [1, 5].

As the resolution ability of photo resists layers is limited by the wave length of light exposed the transfer to X-rays and then to electron beams and electronic resists made possible production of micro scale devices. The methods by which this progress was achieved, advanced photolithography, are rapidly approaching some hard, fundamental barriers. Without a new technological direction, semiconductors and the devices that depend on them will stop becoming cheaper, lighter, and faster. And the new way to meet these goals is nano technological imprinting lithography. Fortunately, there are new approaches that may take semiconductor technology to an even smaller level. This new approach promises to make semiconductor features that can be compared in size to individual molecules and their ensembles. This is nanotechnology indeed.

Functionalized nanomaterials are emerging a key component to meeting these goals. Printing technologies such as ink jet, gravure, flexo, and other graphic arts based systems are being optimized to achieve the higher resolution and operational demands of electronics. In many cases, the unique properties of nanomaterials make them as the necessary components in inks and coatings for these systems and applications. In a part it deals with printed thin film transistors, RFID tags, security printing and functionalized packaging manufacture as well [5]. Thus the era of nanotronics began.

The well known firm Degussa AG organized the research Centre "Nanotronics Science to Business". Prof. Utz-Hellmuth Felcht – the management Board Chairman of this company had clamed in 2005 Year that Degussa will be investing €50 million over four years into the development of innovative, nanomaterials-based solution for electronics application. They organized the Nanotronics Center for that indeed. The company cooperates with many innovative companies, as in printing branch, for which nanotechnology will be playing an important role.

Imprinting Lithography - Micro- and NanoContact Printing. Hopes on the Future

Last time several research groups in industry and academia started investigating "imprint lithography" methods for fabricating small features. The imprint lithography is essentially a micromolding process in which the topography of a template, or mold, defines the patterns created on a substrate. Investigations in the sub-50 nm regime indicate that imprint lithography has almost unlimited resolution.

At the University of Texas, there was developed a room temperature, very low pressure variant of imprint lithography known as Step and Flash Imprint Lithography, or SFIL [6]. This kind of imprint lithography begins by spincoating an organic layer onto a substrate. Then a low viscosity, silicon-rich, UV photo-polymerizable imprint solution is dispensed on the wafer to form an etch barrier in the area to be imprinted. A surface-treated transparent template is used bearing patterned relief structures over the coated substrate. The template is lowered onto the substrate, thereby displacing the solution, filling the imprint field, and trapping the photo-polymerizable imprint solution in the template relief. The quartz template is transparent, allowing for irradiation of the imprint solution with UV light through the backside of the template. After the solution has been cured, the template is then separated from the substrate, leaving an organic-silicon relief image on the surface of the coated substrate that is a replica of the template pattern. The wafer is then stepped and the process is repeated on the next field [1, 6].

Some relative versatile "top-down" method for the fabrication of particles, Particle Replication in Nonwetting Templates (PRINT), was described which affords almost absolute control over particle size, shape and composition (Fig. 5) [7].

Now we can see that new nanotechnologies make available for example the production of semiconductor devices such as RFID tags on and inside of packaging by printing as well as on security imprints. Thus last time there was used a method of marking of nanospots on banknotes among others. Nanoparticles of gold (diameter 60nm) where used for printing the image figure which contained 20 000 nanoparticles (Fig. 6) [8]. It may open new ways in security printing.

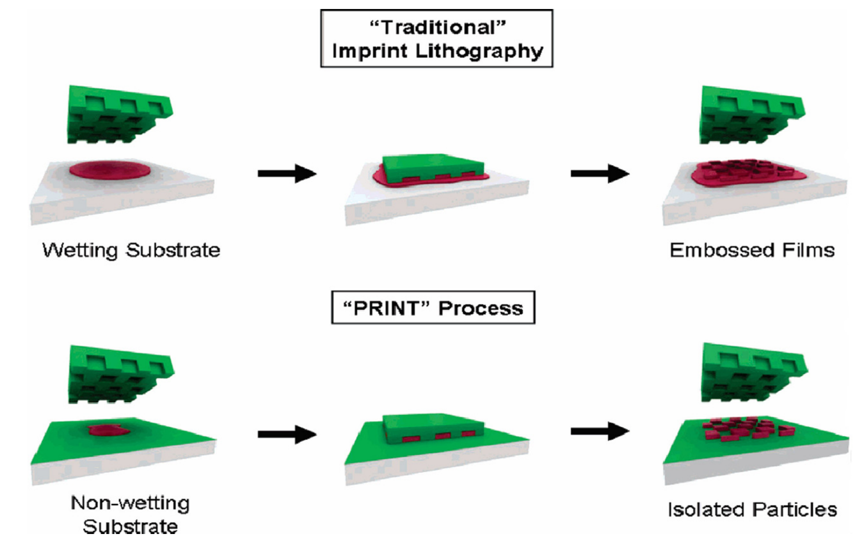

Figure 5: Comparisons of "PRINT" process with "traditional" SFIL imprint lithography. Nonwetting nature of fluorinated materials and surfaces (photo curable perfluoropolyether) permits to form isolated as well as nanoparticles.

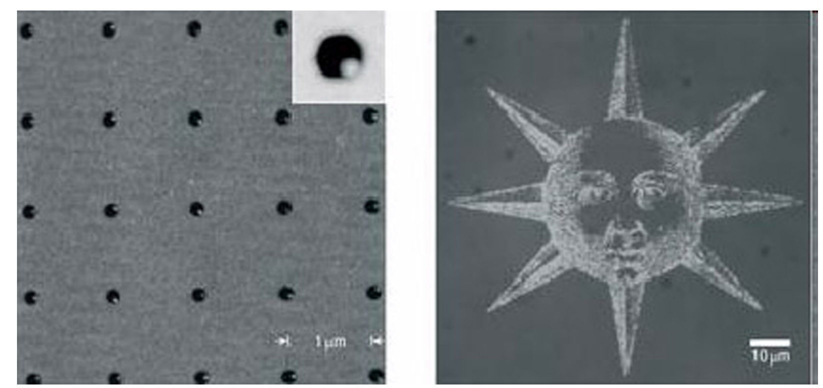

Figure 6: Nanospots on banknotes (IBM laboratory, New Scientist, 2007)

Radio-frequency identification (RFID) is an automatic identification method at all, relying on storing and remotely retrieving data using devices called RFID tags or transponders. An RFID tag is an object that can be applied to or incorporated into a product for the purpose of identification and tracking using radio waves. In the foreseeable future, RFID technology promises to greatly improve an organization's ability to track products, parts or shipping containers and provide an unprecedented view into product life cycles. Over time, the technology may provide companies with the ability to follow a product from the factory floor, to the store, into consumers' homes, and eventually to their ultimate disposal. A part of the RFID technology will be connected with a nanotechnology of producing chips by imprint lithography with micro- and nanocontact printing as was said upper. But already now nanosciences achieved some impressible results for example in nanobiology when biological components are formulated on a substrate by means of printing methods [7, 9] (Fig. 7).

Some investigations of the dispersed systems

Thus there are actual synthesis and stabilization of nanoparticles and photoactive nanocomposites in polymer matrixes and on conducting and no conducting surfaces for their utilization by micro- and nanocontact printing techniques. The sizes of nanoparticles growth arbitrary, or spontaneously as one can see (Fig. 1). The problem of obtaining particles of certain size and geometry is rather important and actual. The nanocomposites stabilized will be perspective in different areas of printing nanotechnologies.

Luminescent compositions may be rather attractive for printing and packaging. Improving of light emission (in photo, electric and magnetic fields) of dispersed compositions and filled polymer composites and nanocomposites is dealt with understanding of the influence of size of particles, value of surface, formation of electron acceptor and electron donor centers on the surfaces. Utilization of nanosized systems opens new possibilities to manage electron processes in dispersed systems such as light emitted devices, magnetic and photo luminescent compositions. Thus studies of influence of a size and the nature of particles of photo luminescent agents, magnetic oxides, other particles upon the properties of nanocomposites and their stabilization are very actually to be done.

The aggregation of dispersed particles during transformation of ink-varnish nanocompositions into fixed prints changes the luminescence parameters. Properties of photo emitting nanocomposites depend upon the nature and parameters of conducting layers. Thus, the fundamental tasks for investigation of influence of these factors upon the efficiency of luminescence and stabilization of the nanocomposites properties are to be considered and studied. That will lead to carrying out the micro- and nanocontact printing methods for wide applications. Such investigations are carrying out in NTUU"KPI" in joint work with L.V.Pisarzhevskyi Institute of physical chemistry and O.O.Chuiko Institute of surface chemistry of the National Academy of Science of Ukraine. Special ink systems were designed for the identification of authenticity of printed matter by the luminescent and magnetic properties of inked impressions.

To design materials of this type, magnetic fluids and luminescent compositions based on magnetite were be used [10, 11]. There was discovered that paramagnetic properties of magnetite particles with luminofor molecules changed at UV light illumination. We studied the luminescent and magnetic properties of iron oxide magnetite systems with applied monolayer or multilayer organic luminophore entities. It was found that the introduction of luminescent substances into general-purpose printing inks causes luminescence quenching by printing-ink curing catalysts. Magnetite particles coated with luminescent substances exhibit changes in the magnetic (in particular, paramagnetic) properties depending on the luminescent molecules nature and the surface pre-treatment procedure. Therefore, at the given stage of the investigation, it was planned to pass to nanosized magnetite particles and their surface modification.

One of the important stages of printing technology is producing the printing plate in classic processes or a stamp in modern imprint lithography in microelectronics. As for nanotechnologies in printing there may be realized probably an interesting approach to use inconvenient properties of nano sized carbon particles in states of oxygenation - the highest extent of wetting (moisten angle $\Theta=5\pm2^{o}$) and hydrogenation – the highest extent of unwetting ($\Theta=106\pm4^{o}$) [12, 13]. It opens a new way for carrying out the planar indeed printing plates for classic offset and waterless offset printing processes.

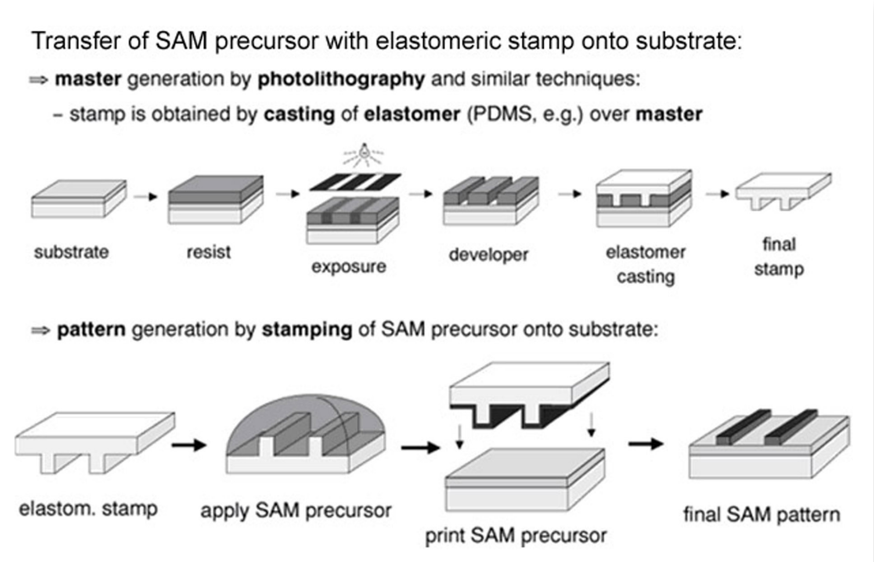

Figure 7: Principle schema of Micro- and Nano Contact Printing. SAM-self assembled monolayer; PDMS – poly-(dimethylsiloxane).

Conclusion

The revolutionary changes in Graphic Arts and printing design of packaging are indeed impressible. The success of digitalization of prepress, press and post press stages of Graphic Arts production is dealt with the progress of electronic industry in a part. These branches are ready to perceive the newest achievements of nanotechnologies. Nanocomposites and nanostructures are used as dispersed systems of narrow nano sized scale in printing processes and materials. A short survey of historical aspects of printing and photographical procedures shows the evolution in development of informational technologies to less and less sizes of dispersed systems in materials and patterns. Micro and nano contact printing came to change photography at all and, in a part, photolithography in microelectronics and now nanoelectronics and nanophotonics. The imprinting lithography promises to decide the challenges in miniaturization of electronic and photonic devices. It will be applied in security printing and producing of packaging with specific electronic tags.

Investigation of various dispersed systems and their using will undoubtedly raise printing and printed packaging to a qualitatively new level including bi- and poly functional nanosized systems as applied to their use in the information technology, technical diagnostics and other areas.

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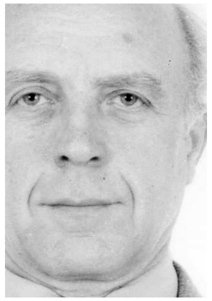

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