ELECTRON BEAM-INDUCED ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION FOR NANOSTRUCTURE FABRICATION

by

Hong Jiang

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Electron Beam-Induced Organometallic Chemical Vapor Deposition

for Nanostructure Fabrication

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SUPERVISORY COMMITTEE:

APPROVED	DATE
Signature	Dec 6th, 2000
Dr. Brian W. Robertson Typed Name	
Signature	12/6/00
Dr. Natale J. Ianno Typed Name	
Signature	12-6-00
Dr. Robert J. De Angelis Typed Name	
Signature	12/6/00
Dr. Jennifer I. Brand Typed Name	
Signature	12/6/00
Dr. Peter A. Dowben Typed Name	
Signature	
Typed Name	

GRADUATE COLLEGE
UNIVERSITY OF NEBRASKA

ELECTRON BEAM-INDUCED ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION FOR NANOSTRUCTURE FABRICATION

Hong Jiang, Ph.D.
University of Nebraska, 2000

Adviser: Brian W. Robertson

I show that nanometer scale metal-containing features can be fabricated in selected areas using non-carbonyl organometallics and a focused electron beam. Nanostructures are fabricated by electron beam-induced organometallic chemical vapor deposition from precursors ferrocene and nickelocene using a field emission scanning transmission electron microscope (STEM). Lines of 4 nm wide with uniform width and smooth surface are routinely obtained using a focused electron beam with probe size near 1nm. *In-situ* investigation for the effects of deposition conditions on the mechanism of film growth has been conducted in the STEM. Substrate temperature and organometallic partial pressure play an important role in the growth mechanism. Two different film growth mechanisms and two resulting structures of the deposited material are found at different deposition conditions. The ratio of organometallic partial pressure during deposition (P_{OM}) to its equilibrium vapor pressure (P_v) at the corresponding substrate temperature is found to be a governing parameter for the film growth mechanism and hence the structure of deposition results. Either uniform deposits with high edge acuity or 3-dimensional nano-network structure can be obtained by selecting a suitable combination of organometallic partial pressure and substrate temperature. The effects of deposition

conditions such as electron dose, hydrogen additive and low temperature annealing after deposition on the deposition results have also been addressed.

Acknowledgments

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I wish to dedicate this thesis to my husband Liming and my daughter "the Naïve One" who understood a graduate student's life and helped me with computer skills, also to my parents Zhiming and Shengzhang who understood my time consuming experiments and took care of my family life.

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CHAPTER 1

Introduction

Patterned electronic and magnetic nanostructured materials have become increasingly attractive in recent years, both scientifically and technologically, for their novel properties [1-11]. Scientifically, nano-sized particles serve as additional means for controlling fundamental magnetic and electronic phenomena such as domain structure, magnetization reversal, quantum effects and tunneling effects. Technologically, nanostructured materials have found applications in information storage, giant magnetoresistance (GMR) sensors, magnetic refrigeration, ferrofluids, color imaging and medical diagnostics. The advantages of scaling device feature sizes to nanometer dimensions are overwhelming since the area per function, the energy needed to switch a device, and the energy needed to be stored to represent information all scale with the physical size of the device, although there are limits. Important new physical phenomena become available for exploitation in electronic and magnetic devices as the feature dimensions are reduced to nanometer regime. As dimensions shrink below 100nm, however, the fabrication of precisely controlled structures becomes challenging. Many nanofabrication techniques have been developed and investigated. The most widely used fabrication techniques are derived from microelectronic fabrication methods and involve a form of lithographic definition of patterned material. In the following sections of this introduction, these and other related fabrication methods are discussed. The final part of the introduction concerns the approach used for the research in this thesis – electron beam

induced organometallic chemical vapor deposition, which will be referred to by the acronym *e-CVD*.

Nanofabrication Techniques

Electron beam lithography

The highest spatial resolution form of lithography developed to date is by scanning probe methods (for example, STM – scanning tunneling microscopy), which will be discussed later. This technique is not widely applicable because of the very slow scan speed, which even parallel arrays of STMs are unlikely to overcome. More commonly used (and still very high resolution) is electron beam lithography [1 - 9, 12 - 21]. This is a multi-step process for each single layer of material. It involves preparation of a substrate, commonly Si, with radiation-sensitive resist, pattern definition in the resist by exposure of the resist either to an electron beam projected through a mask or to a focused electron beam, development of the resist pattern, and post-exposure processing. The post-exposure process includes either lift-off or ion etching as part of an additive or subtractive process, respectively. In additive processing, lithography is used to define the desired pattern in a resist on the substrate, material is deposited after development of resist, and the excess material is then removed by washing away the resist in a solvent (See Figure 1-1). In subtractive processing, material is deposited on the substrate before lithography and the ion-etching step is used to define the pattern in the material layer and to remove the excess material after beam exposure and resist development (See Figure 1-2). Research on electron beam lithography is directed at the optimization of lithography

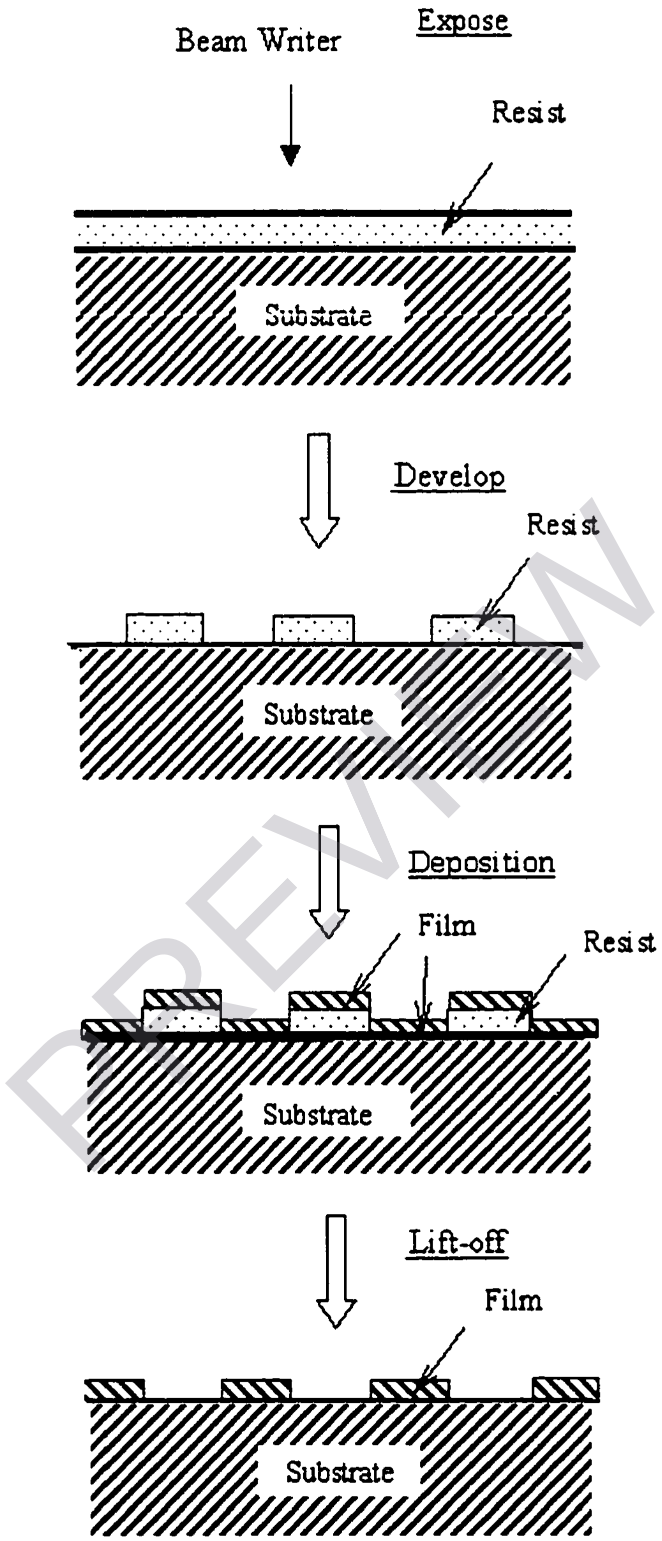

Figure 1-1. Schematic of additive process for lithography.

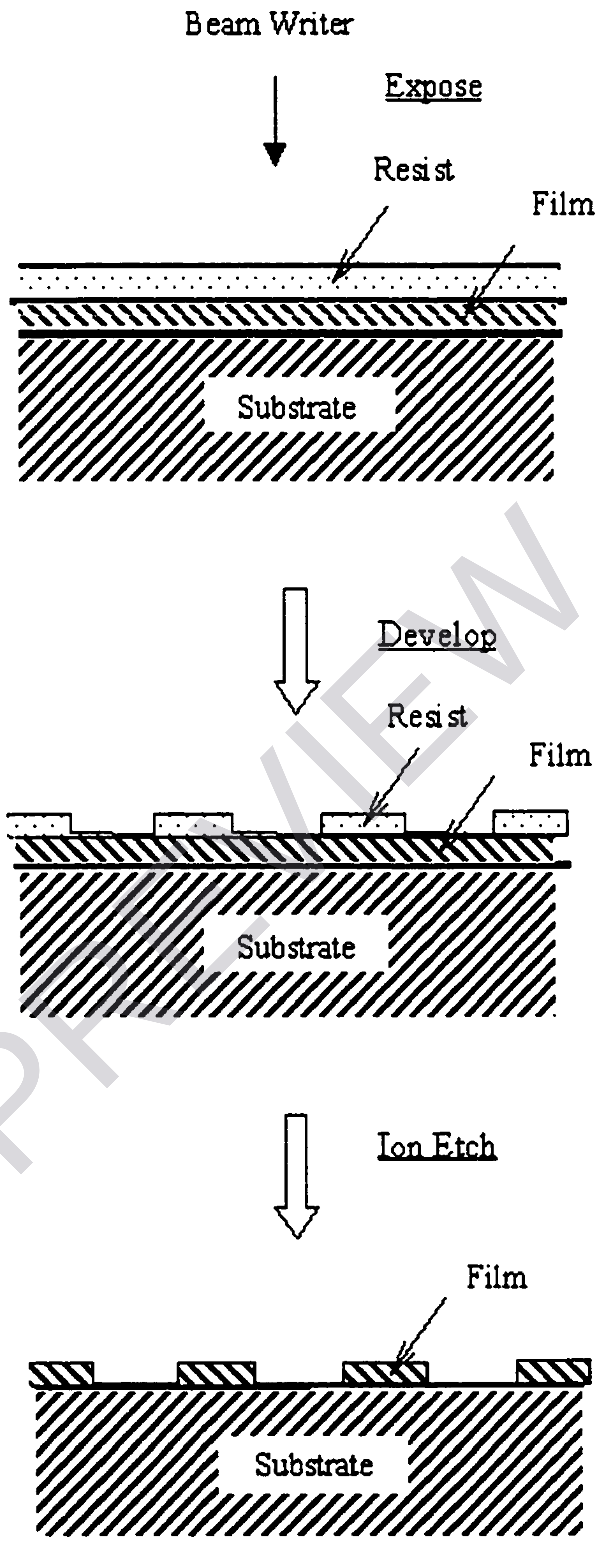

Figure 1-2. Schematic of subtractive process for lithography.

systems, novel resist technologies, pattern transfer techniques and new lithography techniques.

The spatial resolution of electron beam lithography is limited by the electron beam image resolution (or electron probe diameter), by electron backscattering from the substrate, and by the ultimate resolution of the resist, which depends on the size of resist molecules and on the interaction between the electrons and the resist molecules. The feature resolution of the final pattern in the material is also limited by the accuracy of pattern transfer from the resist to the material layer. A resolution of 80 nm is routinely practical.

Radiation-sensitive resists fall into two categories: positive, in which the exposed regions are more soluble, and negative, in which the irradiated regions are less soluble than the unexposed resist. Polymethylmethacrylate (PMMA), generally accepted as a high-resolution positive resist, was the first resist to be developed and continues to be one of the best resists. Line widths under 15 nm have been achieved in PMMA [1, 9, 12, 14, 22]. In experiments to measure the resolution of electron beam lithography techniques [22], hairline breaks were found in metal lines with line width less than 15 nm fabricated using PMMA. The hairline breaks are thought to be due to single molecules of PMMA bridging the lines. It has been concluded that organic resists have reached their limit because of their necessarily large molecular size. Sub-10 nm fabrication has been reported with inorganic resists, such as metal halide salts [12, 23 - 26], metal oxides [27], semiconductor oxides [28] and contamination resists [22, 29].

The spatial resolution is also limited by the interaction between the electrons and the materials the electrons penetrate. As the electrons penetrate the resist, the beam

broadens by small-angle scattering (forward scattering), resulting in a larger beam size at the bottom of the resist. As the electrons pass through the resist into the substrate, they may be backscattered from the substrate and cause additional resist exposure at a significant distance from the regions intentionally exposed. This is known as the proximity effect. Secondary electrons generated by inelastic scattering of primary electrons and backscattered electrons also degrade the resolution by widening the beam diameter. Fast secondary electrons contribute to the proximity effect.

Beam broadening and secondary electron effects can be minimized by using a thin resist, a thin substrate, and a high primary beam energy, because a high primary beam energy results in less beam broadening and secondary electron production. Proximity effects can be minimized by using thin substrates that reduce backscattered electrons. For thick substrates, there are two approaches for minimizing proximity effect: one is to use high enough energy primary electrons ($\geq$ 50 keV) that the resist receives a diffuse extra "fog" dose in a very large area [1, 30, 31]; the other is to use very low-energy electrons to reduce scattering [15]. The penalty in the low energy case is that the resist has to be very thin because the low energy primary electrons penetrate very little into any material. Different techniques of correction or reduction of the proximity effect have been proposed, including equalization of background dose [32], pattern biasing (shape correction) [33], dose correction [34, 35], and multilayer resists (overhung resists) [36, 37].

In a lift-off process, the sample is dipped into a solvent, which dissolves the resist and lifts off the film on top of the resist, leaving behind the patterned film on the substrate. As the line width decreases and thinner resist layers have to be used, the lift-off

process becomes increasingly difficult because of the difficulty of completely separating the material layer that covers the resist from the layer on the substrate. Resolution is limited by the edge roughness, which leads to intolerable variations in line width, and line discontinuity (See Figure 1-3 [38], for example.). For the ion etching process, reactive ion etching, using chemically reactive gases, is usually used to minimize ion damage and to increase anisotropic etching [13, 19, 39]. A major difficulty in shrinking dimensions is therefore the lack of lateral dimension control.

For high-throughput electron beam lithography, a parallel projection technique is used. The technique termed "scattering with angular limitation in projection electron-beam lithography", or SCALPEL, has being developed in Bell Laboratories (Lucent Technology) [40 - 48]. In the SCALPEL technique, scattering contrast, rather than the absorptive contrast employed in other projection electron beam techniques, is used, based on the concept proposed by H. W. P. Koops and J. Grob [49]. In the SCALPEL system, a mask consisting of a thin low atomic number membrane (typically 100 nm silicon or silicon nitride) and a high atomic number pattern (typically 50 nm tungsten), referred to as the scatterer, is uniformly illuminated with high energy (~100 keV) electrons. An aperture in the back focal plane of one of the electron projection imaging lenses stops the scattered electrons and this results in a high contrast image. This image can then be further de-magnified by additional electron lenses (See Figure 1-4 [50]). In the SCALPEL approach, the mask defines the pattern but a mechanical aperture absorbs the energy from the unwanted parts of the beam. The separation of pattern formation and energy absorption minimizes thermal instability of the mask and maintains pattern fidelity. Features as small as 80 nm have been printed in resist using SCALPEL

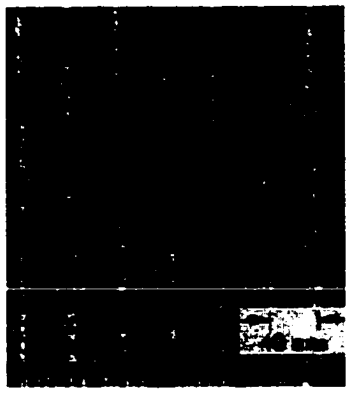

Figure 1-3. Ni/Au grating with a line width of 10 nm and a spacing of 30 nm on bulk GaAs fabricated by electron-beam lithography [38]. Resolution for lift-off process is limited by the edge roughness and line discontinuity.

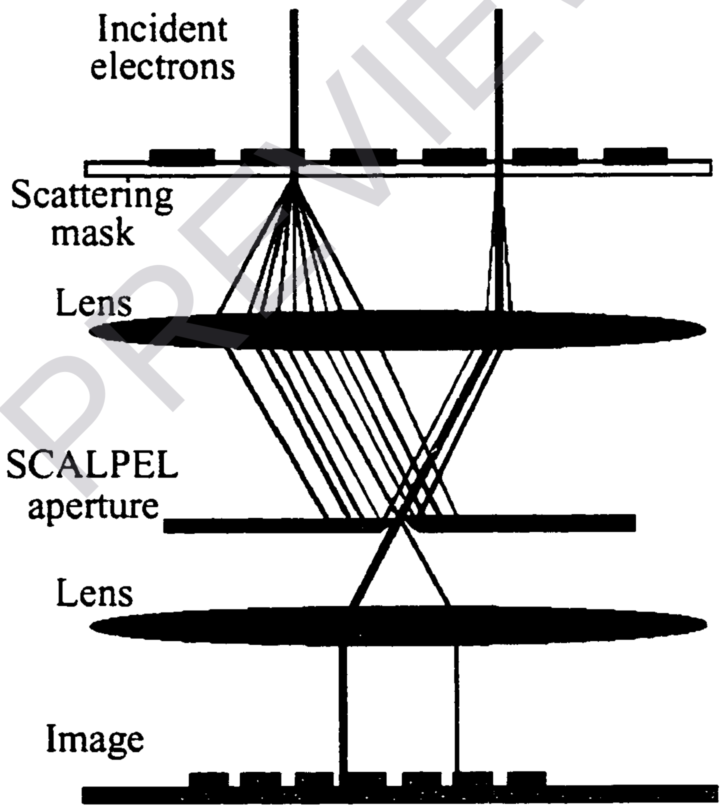

Figure 1-4. Basic SCALPEL principle of operation showing contrast generation by differentiating more or less-scattered electrons [50].

technique [50]. SCALPEL is recognized as a mass production technique for the next generation IC fabrication with throughput that is expected to be comparable with more conventional optical lithography after full development. The challenges in the technique include the fabrication of low-distortion masks and the accuracy of overlay pattern placement.

In electron beam lithography, chemical or ion etching are essential for material removal and cannot be avoided. The associated composition modification and the damage to the deposited material or substrate are unsolved problems. A difficulty of this technique that is shared by other lithography techniques is in achieving both the control of the position of deposits and the accuracy of overlay that are required for nanoscale fabrication to realize ultrahigh-density circuits. The inability to change a pattern after a mask has been fabricated makes this technology an inflexible one.

Nanoimprint lithography

Chou and coworkers have been investigating nanoimprint lithography for high throughput nanofabrication [51 - 55], as have Whitesides and others [56 – 57]. The technique employs a reusable mold fabricated by electron beam lithography or other techniques to imprint patterns at high pressure in a resist that is held at a temperature above its glass transition temperature. Reactive ion etching is then used to remove the residual resist in the recessed regions. This technique reduces the cost but has diminished control of overlay accuracy. It has been used to fabricate large arrays of magnetic bars and pillars [53] and metal gratings [51].

X-ray Lithography

Like projection electron lithography, X-ray lithography has the advantage of speed due to the parallel nature of the process. It has been used for the fabrication of large dot arrays [58]. The x-ray source can either be a point source or a synchrotron. The ultimate resolution is limited by diffraction and less than 50 nm can be achieved [59, 60]. It is not clear whether the technique can be pushed below the 30 nm feature size towards the wavelength limit. The mask is made of a patterned absorber of high-density material (typically gold or tungsten) supported by a membrane of low-density material that is transparent to x-rays. The absorber is patterned by electron beam lithography. The major challenge for x-ray lithography is that there is no pattern demagnification and this places severe tolerances on mask fabrication. Controlling the distortion due to residual stress in the patterned metal on the mask is especially important.

Ion beam techniques

Focused ion beams are potentially the most versatile tools for nanofabrication although the resolution is not comparable with the electron beam cases. An ion beam induces various chemical effects through collisions with target atoms or by the doping effect of the implanted ions. Ion bombardment of a solid surface can enhance adsorption or induce new bonding resulting in decomposition or formation of molecules. Focused ion beams can be used in processes including exposure of resists [61 - 65], ion machining [66, 67], ion induced etching [68], ion stimulated deposition [66, 67, 69 - 81], or selective area ion implantation [82]. An advantage of ions over electrons is in the reduced range of scattering and in the reduced backscattering. Exposure with ions therefore does not cause

such deleterious proximity effects as encountered with electron exposure. In ion optics, electrostatic lenses generally have to be used which have higher aberrations than the magnetic lenses used with electrons. Ion sources have much larger chromatic spread and the effect of particle-to-particle Coulomb interactions is increased compared to those of electrons. The ultimate resolution of focused ion beam techniques is limited by the difficulty of focusing ion beams to dimensions below 10 nm. In addition, ions are far more damaging to the underlying material than other forms of radiation and the elements of the ion beam can quite effectively "dope" a semiconductor. Ion beam techniques do not offer an advantage over their electron equivalents. Their main application is in mask and circuit repair [77, 78, 83, 84], particularly in the removal of unwanted material.

Chemical fabrication methods

There is an increasing range of chemical fabrication methods being developed – driven particularly by their potential in self-assembly methods by which periodically repeated patterns could be fabricated, without the problems of mask making and use, or by which additional features could be selectively attached to certain parts of patterns prepared by other methods, thus eliminating the issue of accuracy in overlay placement. A major limitation is that only chemical fabrication methods that modify a previously patterned substrate are capable of being used in preparing aperiodic structures. Additionally, fabrication techniques such as chemical self-assembly [85, 86], electrodeposition [87 - 92] and chemical synthesis [93] require contact with fluids and subsequent removal from the fluid into an ambient gas. Either of these steps may result in altered surface composition. The accurate control of shape, position and uniformity of the

deposits created by these techniques or by strain-induced self organization [94 - 105] is also very difficult at the nm-scale, although new techniques that make use of periodic surface steps and kinks are under development.

Scanning Probe Fabrication Methods

The highest resolution and most accurate control of deposits have been achieved using scanning probe microscopes (SPM). SPM offers atomic resolution in the region of 1-0.2 nm. The scanning tunneling microscope (STM) and the atomic force microscope (AFM) have been used for many types of material modification: exposure of resists [106 - 118], surface oxide modification [119 - 124], chemical vapor deposition [125 - 133], field evaporation [134 - 137], manipulation of atoms [138 - 140] and nanoparticles [141, 142]. To fully utilize the pattern resolution available with SPM, novel resists, including self-assembled monolayers (SAM) [110, 111, 115, 116] and surface oxides [119 - 124] form an active area of research. However, the scanning probe techniques are severely limited in writing speed and the resist thickness it can expose. Even proposed arrays of scanning probes fabricated as microelectromechanical systems by microelectronic methods are unlikely to achieve high throughput; they will be exceedingly complex to control.

Electron beam-induced OMCVD (e-CVD)

Electron beam-induced organometallic chemical vapor deposition (termed e-CVD throughout this work) is potentially an important technique in nanostructure fabrication. The process involves introducing organometallic source vapor onto a substrate and