Sub-Millisecond Post Exposure Bake of Chemically Amplified Photoresists by CO₂ Laser Spike Annealing

CNF Project # 386-90

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Abstract:

Pattern formation in a chemically amplified photoresist requires a post-exposure bake (PEB) to catalytically deprotect the polymer. Excessive diffusion of the photogenerated acid results in the loss of line edge definition, blurring of latent images, and changes in the line edge roughness. To optimize the process, we have explored sub-millisecond PEB using a CO₂ laser-based scanned annealing system. Several polymer and photoacid generator resist systems were studied under 500 µs laser spike annealing (LSA) at estimated temperatures between 120 and 240°C. All the resist systems exhibit remarkable stability in this time/temperature regime, with the maximum useful temperature limited by thermal deprotection and/or decomposition of the polymer backbone. At lower laser power (temperature), high resolution patterns with sub-100-nm features are formed, comparable to hot plate reference samples. Resist sensitivity is improved significantly for several resist systems (dose to clear is lowered), while other systems exhibit little change in photosensitivity.

Summary of Research:

Chemically amplified resists (CARs) are the current workhorse in lithography for semiconductor device manufacturing because of their high sensitivity and excellent patterning performance. In 1982, Ito, et al., proposed the concept of chemical amplification [1], where irradiation activates photoacid generators and the generated photoacids subsequently catalyze numerous reactions in a resist film before being trapped or quenched. In CARs, acids must be mobile enough within the resist matrix to deprotect sufficient acid-labile protecting groups to achieve the solubility switch in the developing media, but excessive acid diffusion can lead to image blur and loss of resolution. This chemistry occurs during the post-exposure bake, normally done on a hot plate at a temperature of 90-150°C for 30-120 s.

In this work, an alternative post exposure bake (PEB) approach involving higher temperatures for dramatically shorter times has been investigated [2].

Figure 1 displays the chemical structures of resist copolymers and photoacid generators used in this study. With two photoacid generators (PAGs), triarylsulfonium hexafluoroantimonate salts (THS) (50 wt % in propylene carbonate) and N-hydroxynaphthalimide triflate (NI-Tf), to make resist solutions in propylene glycol methyl ether acetate (PGMEA). A formulated and commercially available TOK-EUVR P1123 ME was also used.

Samples were DUV exposed for varying times using a Hybrid Technology Group System III-HR contact/proximity mask aligner at wavelengths of 235-260 nm (measured power of 2.5 mW/cm² at 254 nm) and 405 nm (measured power of 20 mW/cm²). After DUV exposure, the photoresist films were PEB annealed using either a hotplate (115°C/60 s) or annealed by the CO₂-based LSA system at varying powers (temperatures) for 500 µs. Figure 2 shows the latent images on an exposed and LSA annealed photoresist film before development.

With LSA PEB, under DUV exposure at 235-260 nm, up to 3.5 times sensitivity enhancement was achieved for the P(MAdMA-co-GBLMA)/NI-Tf resist system, 0.67 times for ESCAP/NI-Tf, and 3 times for ESCAP/THS, compared to hot plate results. Under 405 nm exposure, up to 5.3 times sensitivity enhancement was achieved for the P(MAdMA-co-GBLMA)/NI-Tf resist system, 3 times for ESCAP/NI-Tf,
and 4.2 times for ESCAP/THS. LSA PEB showed imaging capabilities comparable to hot plate PEB.

In contrast, the commercially available TOK-EUVR P1123 ME resist was also tested at DUV exposure wavelengths. Over a wide range of annealing conditions, the dose to clear showed only small changes and, generally, slightly less sensitivity than hot plate PEB. The sensitivity change in LSA post exposure baked photoresists may be linked to the extremely high thermal ramp rate of LSA (10⁶ K/s, compared to 10 K/s for hot plate) and the extremely short PEB time of LSA (500 µs, compared to 60 sec for hot plate) that can affect the reaction and diffusion kinetics in the photoresists.

To assess the potential for high resolution patterns, electron-beam lithography was done on the TOK resist using Leica VB6. 80 nm 1:1 line/space patterns were achieved for both hot plate (e-beam dose: 17.4 µC/cm²) and LSA PEB (e-beam dose: 43.1 µC/cm²), as shown in Figure 3.

We have demonstrated sub-millisecond LSA as an alternative approach for PEB annealing. In future work, the impact of varying laser anneal dwell time and resist/PAG architecture will be explored. The quantitative determination of acid diffusion rates and activation energies is being carried out using a resist bilayer system (PAG loaded/PAG-free) [3]. Higher resolution imaging and line edge roughness measurement will also be undertaken.

**References:**


Photoelectrical Imaging and Characterization of Point Contacts in Pentacene Thin-Film Transistors

CNF Project # 775-99, 1486-06
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Abstract:
We report the spatially-resolved electrical response of bottom-contact pentacene thin-film transistors to a scanning, focused laser. We find that pentacene films make point-like electrical contacts to the underlying gold electrodes and are able to image them with diffraction-limited resolution. We can further estimate the interfacial resistance associated with hole-injection at an individual point contact, and show that optical activation of one alone increases device current significantly.

Summary of Research:
The performance of organic thin-film transistors has improved significantly over the years [1]. However, achieving efficient charge injection in these devices is a challenging issue [2].

We studied the injection behavior of pentacene transistors with bottom-contact gold electrodes, see Figure 1(a) [3]. Pentacene was evaporated on highly doped Si wafers (220 nm oxide thickness) pre-patterned with 3 nm Cr/40 nm Au electrodes (channel lengths = 10, 20, and 50 µm; widths = 150 and 300 µm). We patterned pentacene using a parylene subtractive etching technique to isolate the devices from parasitic currents. In Figure 1(b), we show typical output characteristics, from which we extracted a hole mobility of ~ 0.2 cm²/Vs. At low source-drain voltages, however, we observed a sigmoidal behavior, indicating the presence of an injection barrier.

We rastered a focused, λ = 658 nm, ~ 100 µW, ~ 1 µm spot size beam across our device, and simultaneously recorded the reflected light intensity as well as the source-drain current as a function of spot position. In the main panel of Figure 2(a), we show a false color current image of a device for V_{DS} = 0, V_{GS} = -20 V with the grayscale reflection image overlaid for reference. The current image exhibits striking spots of opposite polarity at the drain and source contacts. In Figure 2(b), zoomed-in and separated reflection and current images of the boxed area at the drain resolve the spots with greater clarity and reveal that they are located at the pentacene side of the interface.

The effect of zero-bias “photocurrent” generation can be explained by the band diagram shown on top [Figure 2(a)]. While the band structure of the pentacene bulk is made p-type by the gate, the levels are pinned at the contacts, resulting in a potential gradient at the interface. Here, photo-generated carriers separate and induce a current when collected, with sign dependent on the direction of band-bending.

Devices with greater number of spots demonstrate better electrical performance overall. Substantiated by our measurements to follow, this strongly suggests that these spots correspond to good hole-injection contacts.

Furthermore, a line cut of the central spot in the zoomed-in current image is taken along the interface and fitted to a Gaussian with width equal to the laser spot size. If pentacene formed extended electrical contact, we would expect an elongated signal. Instead, we observe point contacts to the gold within instrument limits. Therefore, despite the high pentacene film thickness (~ 50 nm), this gives evidence that hole-injection occurs only at localized physical contacts to the first monolayers.
When a drain bias is applied \((V_{DS} < 0)\), a different effect is observed. At the top of Figure 2(b), we show the current image \(I_{ph} = |I_{light} - I_{dark}|\) for a device with \(V_{DS} = -10\) V. Now, the most striking response is present only at the source, or hole-injecting electrode, for which photo-generated current is two orders of magnitude larger than that at zero bias. A zoom-in of the area in Figure 2(a) is shown in Figure 2d for both \(V_{DS} = 0\) and \(V_{DS} = -1\) V. Their comparison reveals that the same contact points at the source seen from zero-bias photocurrent contribute to the larger signals under bias, suggesting that the laser assists in hole-injection.

Two processes are responsible for this effect. The first is trap-induced photoconductivity, which is effective throughout our devices. Photo-generated electrons can fall into shallow traps with long lifetime and attract additional holes from the source to increase current. In Figure 3(a), we show the laser power dependence of \(I_{ph}\) when the laser is fixed at three positions for \(V_{DS} = -1\) V, \(V_{DS} = 0\): a contact spot at the source (arrow, left inset) and two areas within the channel (midgap and close to the drain electrode). All data show good fits to a power law with subunity exponent \((-0.3-0.4)\), reflecting increased trap filling at higher light intensities.

We plotted the ratios of \(I_{ph}\) for the different positions as a function of laser power (inset). \(I_{ph}\) at the source especially dominates at lower powers and decreases relative to the photo-response at midgap at higher powers. In contrast, midgap/drain is nearly a constant, suggesting a different photoelectrical mechanism unique to the hole-injection contact.

We posit that localized, photo-induced electron traps at the source alter the interfacial band structure. In general, holes injected from gold to pentacene must overcome a depletion barrier region (width \(w\)) where the bands are pinned [Figure 3(b), left]. Previous scanning probe studies revealed that this translates to a large interfacial resistance \(R_i\) that can dominate overall device resistance. Under illumination (right), the generated electron traps act as \(p\)-dopants of pentacene by attracting additional holes, reducing \(w\) and \(R_i\). This is akin to semiconductor devices, where increased dopants around metal are used to reduce contact resistance.

Finally, our studies reveal that pentacene makes point-like electrical contacts to the gold electrodes. When the device is under bias, they become spots that increase current dramatically when optically activated.

References:

Fabrication of Fluidic Structures

CNF Project # 917-00
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Abstract:
A process flow utilizing the newly installed ASML PAS 5500/300 stepper at CNF was found to be capable of transferring features below the optical resolution limit of 248 nm lithography by using electron beam sensitive resist. The PAS 5500/300 was also used to print and verify feature placements with sub 50 nm accuracy.

Summary of Research:
Research involving zero mode waveguides (ZMWs) requires critical dimensions (CD) of 160 nm or less. Unfortunately, this rests at the very edge of the optical resolution limit of 248 nm KrF lithography.

After exploring a variety of conventional DUV resists, we branched our search to electron beam lithography resists and found that high resolution could be achieved with NEB-31A, a chemically amplified resist produced by the Sumitomo Chemical Corporation. The negative tone and poor etch resistance of this resist lead us to experiment with a metal liftoff process which we have developed to print lines and vias with CDs of better than 145 nm.

Chips for calibration of precision optical detection systems require very accurate feature placement accuracy across a large field of view. The extremely low distortion introduced by the image projection system of the ASML PAS 5500/300 at CNF was used to pattern optical alignment chips with a feature placement accuracy of better than +/- 25 nm at 3 sigma across a 10 mm square die.

For verification purposes, an ASML stepper was used to perform metrology capable of measuring this feature placement accuracy across a wafer.
Small-Scale Silicon Wire Device for Biological Sensing

CNF Project # 1469-06
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Abstract:
A small device with nanowires of polycrystalline silicon was fabricated using e-beam lithography. A specific horn shape of nanowire was fabricated to improve the contact with the metal pad. A 5 × 5 µm hole was created in the center of the device to serve as a sensing area, and the rest of the area was insulated to block any conducting path. The two metal contact pads with these nanowires were 10 µm apart, which served as the basis for the electronic sensing. The device characterization was demonstrated with varying gate and drain voltages. Finally, electrochemical impedance spectroscopy was used to demonstrate device-sensing behavior.

Summary of Research:
The motivating force behind the development of nanoscale devices is the fact that they are low-cost, selective, ultra-sensitive, and rapid. However, commercialization has been slow due to various technical difficulties arising in these devices during fabrication and materials. Carbon nanotubes and silicon nanowires have been demonstrated as single molecule biosensors, but the fabrication methods that have been used for creating these devices are typically not compatible with current process techniques, and their integration is technically difficult.

A possible solution is to make the devices out of polysilicon. The aim of this project is to review the fabrication process at the nanoscale by using doped polysilicon as the key semiconductor due to a simple fabrication process. One of the focuses we considered was the electrical properties, materials and design considerations of polysilicon nanowire devices for biosensing application.

Nanowires have particular benefits over carbon nanotubes (CNTs) when used as biosensing devices. First, the properties of the material can precisely controlled. Second, there is a wider class of well-developed fictionalization and blocking chemistries by modifying nanoscale layer outside as well as inside of nanowires. Another huge attraction towards polysilicon nanowire-based biosensors is that they have the potential of achieving ultrafast detection at femtomolar concentration. Several researches have also shown that nanowire devices have superior electrical properties and have better gate controllability than conventional MOSFET.

All nanowire devices were fabricated at the Cornell NanoScale Facility (CNF), Cornell University, Ithaca, NY, USA. The electron transport properties of these polysilicon nanowires are important for understanding the carrier transport mechanism in these nanowire devices. It has been widely reported that crystallized nanowires demonstrate both ballistic and diffusive electron transport mechanisms, depending on the wire length and diameter. Another issue is the nature of the nanowire – metal contact. Depending on parameters such the metal used to make the contact, residual silicon oxide in the contact area, and nanowire dopant concentration, the result may be a Schottky rather than an ohmic contact.

The nanowire has very high resistance, which can be changed using a voltage applied to the wafer substrate. The improved ohmic contact can be seen in our devices (Figure 1) with an Au/Cr nanowire interface as predicted from I-V characterizations (Figures 2 and 3). The device functionality was tested under different pH levels (Figure 4), with the results compiled as a time vs. impedance plot. A 10 mV sine wave was used as device input. Repeatable results from these devices indicate excellent sensitivity and this will serve as a reference biosensing model for ongoing research on bio-agents detection. Our current work is a step forward to address these issues which will not only benefit the fabrication of process but also small in size and would have a huge potential in the future market of polysilicon based nanoscale sensing devices.
Acknowledgements:

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References:


Figure 1: An another well improved SEM image long horn shaped ~ 50 nm wide and 75 nm thin high boron doped polysilicon nanowire separated with 10 µm between two Pt/Cr metal contacts.

Figure 2: Most of these devices show repeatable I-V characteristics with the least variation in nanowire current which is well under 1 µA (for single nanowire) and 6 µA (5 array nanowire). We can easily see from the I-V profile that no Schottky behavior exists in the device.

Figure 3: Gate voltage vs. drain current profile of these medium high doped devices recorded with potentiostat showing excellent gain with small drain to source bias AC voltage (-25 mV to -250 mV) at 503 Hz.

Figure 4: A single frequency (1009 Hz) electrochemical impedance spectra of different pH solution on top of 2-5 nm silicon oxide insulated 50 nm polysilicon nanowire area containing 5 x 5 µm hole in the nanowire center of device. 15.0 mV AC was applied between drain to source electrode with 0.0V DC bias. Higher pH shows high drop in impedance compare to lower pH which indicates clear interaction of ions towards nanowire.
Abstract:
Our group recently developed a novel transfer-free fabrication technique for graphene-based transistors. This process allows for large scale production of devices in an easily automatable fashion by etching the catalytic Cu film beneath the graphene. The resulting device arrays were fabricated with yields approaching 95% and were highly uniform under both Raman spectroscopy and electrical measurements. Our devices also exhibited current saturation at relatively low biases and a promising electron mobility of 700 cm²V⁻¹s⁻¹.

Summary of Research:
There has been considerable interest in the use of chemical vapor deposition as a method for synthesizing graphene since reports employing catalytic nickel [1,2] and copper foils [3]. By modifying the reported method, our group was able to successfully synthesize graphene on Cu thin films. After a standard MOS clean, 285 nm thermal oxide silicon wafers were loaded into an e-beam evaporator. An adhesion layer of Ni (~ 5 nm) was deposited prior to 495 nm of Cu. Samples were then loaded into a hot-walled quartz tube furnace and graphene was synthesized using a modified growth procedure [4]. These graphene films are of high quality, despite the decrease in copper grain size relative to foils. Our fabrication procedure is shown in Figure 1.

Standard photolithography was first performed in order to leave behind a protective layer of photoresist in the shape of our desired final device, after which a 30s oxygen plasma etch was performed in order to remove unwanted graphene. The residual Cu/Ni was then etched in an aqueous solution of FeCl₃. This etch was carefully timed so as to undercut the defined photoresist channel while leaving behind Cu/Ni as contact pads. After carefully flushing with water, substrates were thoroughly dried and the resist was removed. Micro-Raman spectroscopy showed that the devices were highly uniform across the channels as the D, G, and 2D peak intensities and positions did not vary (Figure 2) [5].

Using this technique, we were able to fabricate large arrays of devices simultaneously. For a variety of graphene channel lengths and widths (on average 5 µm in length and 30 µm in width), we observed yields as high as 97%, with nearly 80% of all devices in one particular batch having resistances of less than 10 kΩ. We were also able to fabricate very large...
graphene ribbons, as long as 0.3 mm, with a surprisingly low two terminal resistance of ~ 27 kΩ.

One shortcoming of the chemical vapor deposition route to obtain graphene is the difficulty in using the underlying Si substrate as the backgate. We suspect the reason for this is that products of the copper etching process can become trapped between graphene and the thermal oxide layer, screening graphene from the effects of the Si backgate. One solution to this problem, which we employed to characterize our devices, was to fabricate field effect transistors in a top-gate geometry. We evaporated a thin layer of SiO₂ on our substrates after the graphene channels were defined, and then fabricated individually addressable top gate electrodes. This was done with standard photolithography and evaporating a Cr (5 nm) / Au (45 nm) metal layer. An image showing an array of top-gated transistors is shown in Figure 3.

Our estimated mobility value was significantly smaller than the one reported by Li et al. [3], but it was smaller only by a factor of two in comparison to the mobility reported by Meric et al. [6] for exfoliated graphene used in a similar device geometry. The latter study also reported current saturation and large transconductance. We observed similar current saturation at low VDS and we measured a transconductance of at least 8 µS per 1 µm of channel width. The use of a thinner and more efficient top gate oxide would have likely increased this value by a factor of ~ 20, thus obtaining comparable values to those reported by Meric, et al., [6] for exfoliated graphene.

We note that the single layer graphene synthesis and fabrication method discussed here does not involve any delicate liquid transfer steps, so this method can be easily streamlined and automated. We anticipate that additional work on the synthesis method will improve the electrical and physical properties of single layer graphene from chemical vapor deposition methods.

References:
Abstract:

A microfluidic device is fabricated to characterize the streaming electrokinetic potential on the surface of charged electrospun nanofibers. The electrodes are made of evaporating with Ti and Au on an insulator, Pyrex® wafer, and are covered by a PDMS microchannel to form a microfluidic channel. The cationic or anionic charges of the electrospun charged nanofibers on the electrodes are interacting with the counter ions in the buffer solution. A voltage changes are traced by a source meter during the flow of buffer solution into the channel and the electrokinetic potential of the charged nanofibers is calculated, which is brought about when pressure-driven flow in a microchannel forms double layer ions.

Summary of Research:

It has been commonly known that nanofiber surfaces are chemically and biologically modified to make functionality on them, in order to apply for bio-analysis; such as sample purification, and detection as acting on nano-guiding lines within the microfluidic channel [1]. The nanofibers can be electrospun, arranging them across the microchannels, or along the microchannels in order to create distinct immobilization strings within the channels, or to function as guiding structures for cell movement (see Figure 1). The preliminary studies of nanofiber applicability are provided to conduct the functional investigations as biofunctional guiding structures in microchannels, as biological separators in sample clean up and analyte concentration steps, and also for enhanced immobilization of biorecognition elements. The nanofiber density in the microchannels before and after fluid flow is quantified in order to determine the durability of nanofibers within the microchannels.

The nanoscale particles having carboxyl, sulfon, or amino groups have been incorporated into electrospun fibers to create the functional and bioactive sites on the fiber surface. These particles intrinsically have their own charge potentials according to the buffer solution. The extremely large specific surface area of nanofibers maximizes the availability of functional groups bound on the surface of the electrospun fibers.

The particles are mixed into the mother polymer spinning dopes such as poly vinyl alcohol (PVA) or poly(lactic acid) (PLA), which are then jet to form the nano-scale fibers.
by electric static force. All conditions of electrospinning, the concentration of base polymer in solution, and the ratio of base polymer to particles are optimized to form good morphology of electrospun fibers. Figure 2 shows the schematic diagram in which the fibers have functional groups on the surface. The functional groups on the fibers are characterized to verify that the groups are imbedded or bound into the fiber or the surface of the fiber; using FTIR, XPS and H-NMR, respectively.

Fibers with surface charges have been electrospun directly on the electrodes composed of microfluidic devices to measure the zeta potential on the fiber surface. A microchannel device is fabricated with the electrodes and PDMS channel. The nano-size fibers are electrospun between the two electrodes in order to characterize their charged potentials by measuring the streaming potential generated in the channels during the flow of buffer solution and then converted into zeta potential defined by Smoluchowski [2].

The dimensions of microchannel device are as followed; 2 mm in width, 5 mm in length, and 165 µm in height. In the case of electrodes evaporated by Ti and Au, the distance between two electrodes is 3 mm and the height is 100 nm. Figure 3 illustrates the overall system for the present study. The electrokinetic changes in the surface of the electrospun fibers are being studied by measuring the streaming potentials and the streaming resistance in the microfluidic while a micro pump is flowing the buffer solutions into the channel by varying the flow-rate. Figure 4 shows the results that the changes of voltage are traced during the flow of buffer solution.

The present research will be able to enlarge its initial work into the advancement of sensing fiber technology for advanced materials. As the fabrication of the charged potential electrospun fibers is achieved, the charged electrospun fibers have ability on the immobilization of biological molecules without additional chemical reactions and will progress the development of coordinated biosensing in which 3D biosensing structures have enhanced capability due to simulation of the 3D structure of the original biological system [3]. As the amount of charged potentials on the electrospun fibers is characterized by utilizing the streaming potential at the microfluidic channel, the charged potential of electrospun fibers will be designed by varying the contents of charged particles or types of charge for the final purpose of analysis.

References: