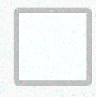
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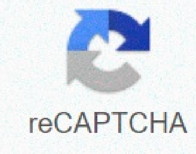

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HEARINGS 6 PAGES + PRESENTATIONS 11 PAGES + PRESENTATION Volumes 11, 2016, Page 211-222It ionizes resistances to chemically amplified eUV lithography using 91.6 eV-powered photons, produces secondary electrons and provides acid-producing electron-driven reactions in a photodiren with chemical amplifier. It is very important to use existing photons efficiently. Unlike DUV lithography, where photons are selectively used by photoactive compounds, 13.5nm wavelength photons ionize almost all materials. However, certain elements have a significantly higher atomic photon absorption cross section at 91.6 eV. To increase photoemilim, sensitive molecules containing highly absorbent elements can be added to photo-mukaramama formulations. These sensitizers have increased in sensitivity in recent years and have lost interest. But there is little experimental evidence that improving sensitivity is only due to higher absorption, since adding metal salts to resistance formulation can trigger other mechanisms, such as changing the dissolution rate, potentially affecting patterning performance. In this study, we used different sensitivitizers in chemically reinforced resistance. We experimentally measured the absorption of EUV light, acid yield, dissolution rate and patterning performance of resistances. Surprisingly, the absorption of EUV resistance was reduced by the addition of metal salt sensitivities. Nevertheless, resisting with the sensitizer showed a higher acid yield. Sensitizer acid helps achieve higher PAG conversion, especially due to an increase in secondary electron production. The patterning data confirms a significant sensitivity improvement, but at the expense of roughness deterioration in high sensitivity. This can be explained by the chemical distribution of the susceptible in resistance, along with a modification of the dissolution contrast, as observed by the dissolution rate monitor. CASES 6 PAGES + PRESENTATION 20. These personal computers were not in a small part defined by two basic types of electronic components: micro-processor and dynamic random access memory (DRAM). These components are both types of silicon integrated circuits, thanks to their existence and increased power to new advances in the manufacturing technology used to create them. In the mid-1980s, computer chip makers were pushing the boundaries of miniaturization using a variety of innovative manufacturing applications. The rise of the digital age depends on new materials and techniques that can improve both performance and drive Cost. For decades, the semiconduutic industry has used photolithography to create integrated circuits on wafers cut from large single crystals of the silicon element. In the patterning process of photolitography, polymer film called photodirenç is deposited on top of a thin film of one of the various materials that have deposited on the silicone wafer. Then, in a complex (and expensive) device known as an exposure tool, a very special wavelength light is projected onto the photodirench with a pattern-bearing mask. photodirenç regions exposed to light suffer chemical changes, making them more or less susceptible to being removed during later chemical development (depending on the process). Thus, the pattern of the mask is transferred to the photodirenç. The pattern from the photodirenç is then transferred to the underlying thin film with a subsequent process of chemical engraving. This fine film patterning process produces multiple iterations, integrated circuits, along with many other physical processes. It's at the heart of the photolithographic process, just as the film is the turning point in photography. In the late 1970s, photolitographic procedures used light from close ultraviolet (UV) and medium UV ranges as 365 and 313 nanometers (nm), respectively. Manufacturers realize that a shorter wavelength movement, supposedly deep UV, 248 nm or less, will allow smaller patterning of integrated circuits, so that the dynamics of miniaturization will continue, superanne increases in functionality, and dramatic decreases in cost characterized by Moore's law. Making a deep UV jump will require dramatic material innovations and a sea change in photodirenç technology. In the early 1980s, an entirely new genus of photodirenç chemically reinforced (CA) photodireners created at IBM for this purpose only would eventually dominate global semiconduur production. More recently, chemically reinforced photodireners have continued to provide moore's law, which was set to light in the later generation of 193-nm. For nearly two decades, CA photoresists have stood behind the digital age, largely unrecognized and unfairly so. Pushing boundaries at IBM Some commentators describe the digital computing business in the late 1970s as split in two, with IBM and all other companies on one side. Despite evolving competitors in the minicomputer industry and the appearance of early personal computers, IBM dominated the computer industry by offering a wide range of host and mid-range computer systems, largely produced by prisoner suppliers within IBM. Large semiconduc manufacturing operations in East Fishkill, New York, and Burlington, Vermont (among other locations) produced integrated circuits as logic and memory components. Most of these semicondule materials Plants, or fabs, came from additional operations in Eastern Fishkill. A disk drive manufacturing plant in San Jose, California, has a research lab. East Coast, Yorktown Heights, New York, became the site for the company's research and development center. Throughout the 1970s, IBM produced its own photolithography equipment. But as the decade came to an end, IBM began buying a significant number of sophisticated and expensive optical devices from outside, especially the revered optical house and Micralign lithography tools manufactured by chemical instrumentation manufacturer PerkinElmer. IBM's manufacturing facilities for advanced semiconducline components included homeowners who housed self-owned and PerkinElmer's self-made and perkinElmer-produced lithography tools. These capital goods represented an enormous expenditure, each vehicle costing hundreds of thousands of dollars. Over the same period, the fate and future benefit of these existing tools were seriously questioned within IBM. Without the launch of 16K DRAM production in 1977, semicondug memory was on track to displace magnetic core memory as the dominant memory technology for digital computers. DRAM's were considered shining examples of large-scale and even very large-scale integrated circuits, where a large number of components were compressed into small silicon chips using the latest manufacturing technology, providing expanded memory functionality at reduced costs. Magnetic core memory, by contrast, greeted from the 1950s, and at each intersection consisted of large grid-like planees of wires with small metal rings: think screen in a window, with a miniature washer in every small square corner. The magnetic states of these rings, or nuclei, represent the digital language of zeros and one. First introduced in 1970, DRAM's outperformed both performance and cost cores after just six years. DRAM's success depended on the semicondug industry's ability to push production technology to the limits. Indeed, DRAM production was bellwether for this technology. The Intel-led semiconduct industry had created a metronomic model where it launched the next generation of DRAM every three years, four times the capacity of the previous generation. Each generation, thus creating a fundamental link between DRAM generations and production technology, required a new level of miniaturization. A question that beflasted for the semiconduc manufacturing industry in 1977 was whether existing lithography tools for 16K DRAM production could be re-used for upcoming 64K DRAM production, or perhaps even for 256K DRAM production. The ability to create smaller properties depends on the wavelength of light used in the vehicle: the smaller the wavelength, Property. Existing lithography tools used 365 nm of light in the immediate UV region to reveal patterns for silicon wafers coated with photodireners. Can existing lithography tools and photodireners be modified to work with smaller light wavelengths? The economic outcome of the answer was significant. Millions of dollars could be saved if the lifespan of production equipment could be extended. 313 Extending the life of IBM's lithography tools and photodirens was a major problem that C. Grant Willson absorbed when he joined a focused research group on polymer science and technology in IBM's San Jose operations. Willson, a Bay Area native, had won a PhD in organic chemistry from the University of California, Berkeley, and worked at the University of California, San Diego, doing biochemistry research. Although it is generally accepted that significantly lower wavelengths in semiconductural society will eventually be necessary to get the necessary miniaturization, the San Jose polymers group was researching the near UV lithography extension for generations of upcoming DRAM. IBM researchers saw an opportunity to expand the usefulness of their tools by moving to the intermediate wavelength, a halfway point between the current near UV and the deep UV in the future. The appeal of this intermediate step was savings: they resisted the fact that they could postpone the need to re-suit factories with new vehicles and knew it would eventually be necessary for the deep UV regime. Furthermore, researchers will buy time to combat more radical developments that will be necessary for the eventual migration of this intermediate wavelength step-365 nm 313 nm- deep UV. Willson's first major achievement in photodiren was to develop a modified version of the standard UV photodirenç type, known as DNQ-Novolac resistance, but set to work with 313-nm light and compatible with existing lithography equipment. Willson's proprietary elbow was used for both 313-nm and traditional UV close lithography, and in a few years ibm semicondugi production was sufficient. Resistance extended the utility and device performance benefits of IBM's existing tools through successful miniaturization, ingring IBM a competitive advantage in the form of enormous cost savings. Willson founded himself as a photoresists leader within IBM. By 1979, Willson was focusing on a more challenging prospect: switching to deep UV. By this time, IBM had been waiting for the delivery of new PerkinElmer lithography tools to the fabs-PerkinElmer Micralign 500. This tool is used in a mercury lamp produced in UV radiation with density peaks of 365, 313 and 248 nm. The use of a suitable filter has made the tool ability to run at any of these wavelengths. The wavelength of 248-nm was in the deep UV zone. This wavelength lamp emanates only 1/30 light amount as in other UV regions. This relative dimness would explain the serious challenges. Existing photodireners did not have enough precision to work at such a low density. A solution-around was made possible by unprecedented long exposure times, but this was an economic nonstarter. Grindingly slow fabs destroy any savings extending to vehicles. Ibm researchers had two remaining options: creating a new lamp for vehicles that were 30 times brighter at 248 nm, or inventing a photodirenç 30 times more sensitive to the 248 nm light that DNQ-Novolac resisted. Chemical Solution Willson focused on the chemical problem: can it create a new photodiren with 30 times precision? Willson discussed this with a visiting scientist who joined his group in the early days of 1979: Jean Fréchet. Born in France, Fréchet was a successful polymer chemist on paid leave from the University of Ottawa at IBM in San Jose. In the discussions between Willson and Fréchet, the essence of the necessary newness emerged: chain reactions. They imagined a photodirener in which a single photochemical event -- the absorption of a photon by a substance in resistance -- could create a cascading chain reaction. Photo-resist chemistry wants to increase the impact of the photochemical event, their goal is great precision yield. Fréchet quickly developed a specific polymer as a possible candidate for use in such a system: polyphthalaldehyde (PPHA). This polymer chain is unstable at room temperature; its tendency is to unzip, depolimerize. The only way to fix the polymer at temperatures up to 200°C is to cover the chain with a chemical group. Both polymer chain and closing groups are highly sensitive to cleavage by acid. Fréchet and Willson assessed the possibility that PPHA could be depolimerized by directly breaking the ligaments in the backbone of the polymer of the irradation. Once started, the polymer is unsip in a chain reaction. Fréchet synthesized PPHA samples so he could start working with Willson and him. However, in the summer of 1979, it became clear that the project might not be completed until Fréchet's permit was expired. At Fréchet's insistence, Willson took a recruiting trip to the chemistry department of the State University of New York's College of Environmental Science and Forestry in Syracuse. There, Willson Hiroshi Ito met with a research assistant in his department with a PhD in polymer chemistry from the University of Tokyo. Ito, like Fréchet, had experience with the special techniques necessary to synthesize PPHA. Willson offered Ito a postd doctoral position in the San Jose group, and in the summer of 1980 Ito joined the lab. Ito took over where Fréchet left off. To produce a warmer polymer by synthesizing ppha in new ways. Ito PPHA teleported, and the result was more fizzle in a chainretion: there was depolimerization, but it's not enough. Ito's next move was to mix a well-known photoacyte generator (PAG) into its ppha and expose the mixture to deep UV light. PAGs are acid-producing compounds when exposed to light. Because both the PPHA chain and the closing group can be separated by acid, Ito thought PAG could initiate the desired chain reaction. This time the PPHA half is zipper-free. That's much better, but it still wasn't good enough. Meanwhile, a new class of PAGs based on onium-salt compounds has recently emerged from 3M and General Electric. These onium-salt PAGs produced especially strong acid, and many had additional virtue of stability at high temperatures. The potential for this new PAGs for polymer chemistry is wide, and PAGs has quickly produced interest. Remarkably, Willson Ito General Electric alighted on PAGs I learned about 3M PAGs at almost the same time. Ito was looking for another PAG to add PPHA-one more temperature stable and produced stronger acid than traditional PAGs. At General Electric, chemist James Crivello invented trihenylsfonium hexafloroantimonate (TPSHFA) for UV-induced polymerization or epoxy resins. This ounce of salt produced a strong acid that catalyses polymerization. Ito was hoping that his PPHA photodirenç system would initiate a strong chain reaction of onium-salt PAG unzipping. Willson recalls the day he tested his novel mix of PPHA and Crivello's PAG as a deeply UV photoresist in the first deep ito. Willson remembers that the results were extraordinary. With a dose of new onium-salt PAG and UV light 100 times less intense than traditional photolithography used, PPHA is quickly and completely zipper-free. Not only did the ingredients unzip, but the Ito mixed areas were also completely evaporated, laying the bare underlying substrate. Ito's material was dramatic evidence of the concept of a chemical amplification scheme that Willson and Fréchet had advanced the previous year. A high-resolution material in the hand (ability to produce fine patterns), high speed, and highly improved sensitivity to deep UV radiation. But the Ito PPHA system worked very well and is not good at all. Evaporated photodirenç material desperately contaminates lithography instruments. In addition, PPHA acid sensitivity acidic engraving procedures offered little protection and therefore had little use in real device manufacturing. Ito's material was dramatic evidence of the concept of a chemical amplification scheme that Willson and Fréchet had advanced the previous year. Willson and Ito headed for another polymer owned by Fréchet. Poly (p-hydroxyxythyne) or PHOST at IBM San Jose during his vacation in 1979. PHOST is a syringe-based polymer chemically similar to Novolac resin used in conventional photodireners. Willson recommended replacing the polymer to include a new side chain: the sexillal butoxycarbonyl, or tBOC. The resulting polymer was poly (p-t-butiloxycarbonyloxystyrene) or PBOCST. Willson, who worked mainly in biochemistly before joining IBM, was aware that tBOC, a mainstay in peptide studies, was prone to division from the base polymer with both heat and acid effect. Willson and Fréchet remember early, make willson and several colleagues resist a PBOCST based on acid catalyzed division of tBOC groups using light-sensitive ortonitrobenzyl esters to produce acid in inept attempts. From Ito's point of view, he was asleep when he reached the PBOCST lab. However, Ito has also begun researching a different tBOCprotected polymer photoasitcatalized cleavage as a potential basis for resistance to chemical amplifier. Looking at Ito's results, Willson and Ito decided to take a hybrid route: mixing PBOCST with ounce-salt PAG. The result of this mixture, which stemmed from the experience and interests of Fréchet, Willson and Ito, stopped the researchers. TBOC displayed dramatic chemical amplification. After resisting TBOC 248-nm deep UV light, the resistant silicone wafer is heated in the oven after exposure. The acid produced by onumni salt catalysed the division of tBOC groups. The resulting parts then produced additional acid, catalysing more tBOC cleavage than a

cascade of de-protection. The reaction was both extremely fast and extremely sensitive to deep UV light. At the beginning of his quest to resist, Willson knew he needed a 30-fold improvement in sensitivity to traditional resistance. TBOC resisted, Willson, Fréchet, and Ito produced 100-200 times improvement. By 1983, Willson was confident enough to promote it within IBM in the new tBOC. In East Fishkill, he presented to a collection of researchers and engineers from various IBM sites, including representatives from East Fishkill's own photodirenç operation and staff from the state-of-the-art fab in Burlington. John Maltabes, a lithography engineer from the Burlington plant, had helped develop a manufacturing process for 1M DRAM using deep UV radiation to meet a 1 micron design rule. Deep UV lithography will be used to produce properties as small as 1 micron on the new powerful memory chip. Maltabes is considering the possibility of replaceing mercury lamps inside PerkinElmer lithography vehicles in Burlington with excimer lasers. However, Willson's tBOC presentation will make Maltabes new It was a better strategy with the mercury lamps available: when he returned to Burlington, Maltabes tried to convince his auditors to kill his project. Three months later, they did it. Maltabes' new job will be to help implement tBOC resistance for the production of 1M DRAM. Is there something in the air? IBM invested the future of its latest products in CA photoresists. The advantages were enormous: tBOC resistance could have saved IBM millions of dollars in replacing and replacing existing lithography tools. The downside was the uncertainty that the new resisters would work in an active production environment. But production trials in Burlington revealed new and unexpected problems with CA resistance. First, its sensitivity changes greatly. By wearing new, meticulous filters, eliminating lithography tools as the source of this unpredictability, the blame is entirely on resisting the tBOC. Eventually, Vermont manufacturing engineers resorted to the kind of highly empirical land magic applications that characterized semiconduutical manufacturing in its early years. They didn't know why some things worked. Engineers found, for example, that allowing tBOC-coated silicon wafers to resist at the factory for several hours before being spoiled balanced sensitivity, but at a lower level. In the top layer of more uncomfortable tBOC resistance, their skin formed from time to time. These skins were photodirench regions where sensitivity collapsed catastrophically. The exposed areas that resisted close to the surface formed a skin that could not develop properly and thus could not be removed by the solvent. Surprisingly, all of these skins were on the surface of resistance. The areas that resist just below these skins are perfectly developed. The problem was serious: these skins cause fatally defective DRAM. IBM invested the future of its latest products in CA photoresists. Groups in San Jose, Burlington and East Fishkill were disturbed by the difficulties of the new resistance. Maltabes recalls a lunch talk about these issues, which a researcher with experience producing disc-drive systems in San Jose suggested was caused by something in the air. This researcher and his colleagues had connected some failures of disk drive systems to air-transmitted pollutants and used activated coal and HEPA filtered air filt filtering systems to overcome the problem. The over-filtration units sat in a warehouse and presented them to the tBOC team. Maltabes and Scott McDonald of Willson's team returned to this ratington with more units. Double with a series of experiments, filtered air environments and air media pumped from outside the fab and the sensitivity to resist was both high and consistent. Fab himself housed pollutants responsible for problems with resisting the tBOC in the atmosphere. With pressure mounting to get 1M DRAM into full production, Burlington decided to filter the air instead of hunting for unknown pollutants or pollutants. After the wafers were covered with tBOC resistance, they stayed in a filtered air environment until they entered the lithography instrument. By 1986, 1M DRAM production continued at full speed. IBM has produced several million of these DRAMs, all of which depend on countering ca tBOC. Reflecting TBOC's criticality to this project's success in moving IBM to its first deep UV manufacturing technology, the firm ensured that tBOC was resisted as a proprietary material and that filtered air was used as a closely held trade secret until the early 1990s. Several million DRAm working within IBM's flagship computer products offered a powerful statement: the CA photoresists era had arrived. For Coda IBM, having the first CA photoresist provided a significant competitive advantage. But in the mid-1990s, a combination of accidental and systematic factors is ibm's special hold on this class of materials. Willson, Fréchet and Ito had patents to resist the tBOC in 1982, but the patent was limited to a CA photoresist too much idea, not just tBOC material. This limited scope was the product of multiple factors: the great role played by researchers rather than lawyers in writing; whims of the process patent compared to patents on certain materials; and previous art discovery in the patent process. One of the developers of 3M onium-salt photoacyte generators, George Smith, previously patented a photoresist that included a very similar mechanism to resisting the TBOC. These accidental factors allow commercial photodirench manufacturers inspired by IBM's success to launch their own versions of CA deep-UV in the early 1990s. More systematically, CA photoresists have fled IBM as the computer giant has joined the growing trend among semiconduer manufacturers to obtain materials from manufacturing equipment and private external suppliers. As IBM began to rely more on lithography tools manufactured by foreigners, the close grab of the vehicle with resistance not only means that vehicle manufacturers need access to the best CA resistances, but also that other customers of vehicle manufacturers will need access. In addition, private photoresist homes ca had more resources and incentives to push photoresists forward. In the mid-1990s, IBM actively passed on second- and third-generation CA photodireners developed by Ito and others to the outside world. Ibm, in this case, accelerates future developments in the CA, of the digital age. 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