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Selective area deposition of boron on Si(111) induced by synchrotron radiation

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We have performed the first deposition of boron on Si(111) induced by broadband synchrotron radiation (SR). Contamination-free thin films were grown at room temperature using decaborane ($B_{10}H_{14}$) as the source gas. After deposition the films were examined using photoelectron microscopy, which showed that film growth was limited to the region illuminated by SR. The temperature of the substrate rose less than 10 K. These results indicate that gas-phase excitations are not important and that the films are deposited by a nonthermal, photoinduced mechanism. Masked exposures demonstrate the potential of this technique for patterned deposition.

Photoassisted chemical vapor deposition (CVD) has shown considerable potential as an alternative to more conventional techniques for growing thin films. Most previous work in this area, including the first deposition of boron from decaborane ($B_{10}H_{14}$),[1] have employed lasers as the excitation source.[2] Although lasers have been very successful, there are a number of applications where the use of higher energy, x-ray synchrotron radiation (SR) is desirable. Laser CVD often involves considerable substrate heating, and the photon energy is often insufficient to break all the required bonds in a single photon process. These problems are overcome by the use of x-ray SR, which offers the added potential advantage of improved pattern definition due to the shorter wavelength of x rays. For parallel processing of submicron features at low temperatures, SR may be the excitation source of choice.

Recently it has been demonstrated that SR can be utilized for thin-film deposition or etching.[3–6] These studies have been directed toward the characterization of the rate, composition, and localization of the process on various materials. Boron is the most common dopant for *p*-type Si. It has been shown that atomically sharp doping layers (δ doping) in Si may be created by annealing adsorbed decaborane[7] or heavily doped Si.[8–10] Thus, a primary motivation for the present work is the anticipation that it may eventually lead to selective area doping using SR CVD, as has been done previously with lasers.[11]

Here we present the first use of SR to deposit boron on Si(111). The experiments were performed on two different beamlines at the Synchrotron Radiation Center (SRC), University of Wisconsin–Madison. SR CVD experiments were performed on the "white light" beamline, which consists of an ellipsoidal mirror which focuses the broadband SR to a spot of $\sim 1.0 \times 0.15$ mm. Flux characteristics of this beamline have been described previously.[12] Deposition was performed with the substrate located slightly past the focus which resulted in a larger illuminated area ($\sim 2.5 \times 2.0$ mm), thereby limiting substrate heating due to absorption of the SR to less than 10 °C. The initial film formation was monitored with white light SR Auger electron spectroscopy (AES).[3] AES measurements were performed simultaneously during deposition using a single-pass cylindrical mirror analyzer and the SR as the excitation source. Use of the SR as the radiation source enabled us to insure that only the exact area where the deposition occurred was analyzed, and also eliminated possible contamination from the hot filament of an electron gun usually used for this purpose.

The *p*-type (10 Ω cm) Si(111) substrate was cleaned by repeated cycles of Ar ion bombardment (500 V) and annealing (1000 °C) until white light SR AES revealed no oxygen contamination and $<5\%$ carbon contamination. This procedure is expected to result in a 7×7 reconstruction of the Si(111) surface. The decaborane (a solid) had been prepared previously by subliming to separate the material from cellite (a stabilizer) and other impurities. Decaborane has a room-temperature vapor pressure of several Torr. The gas was leaked into the ultrahigh vacuum (UHV) chamber (base pressure $= 2 \times 10^{-10}$ Torr) until the chamber pressure was raised to the desired level. A constant flow of gas was maintained through use of a turbomolecular pump.

Figure 1 shows a series of AES spectra taken during boron deposition with a decaborane pressure of 5×10^{-8} Torr. The initial spectrum (bottom) shows the presence of essentially one feature at 92 eV, which is characteristic of unoxidized Si. With increasing exposure to the decaborane and the SR, a new feature appears at 179 eV, which is due to the growth of boron on the surface. After 15 min of exposure at an avearge beam current of 69 mA (total ab-

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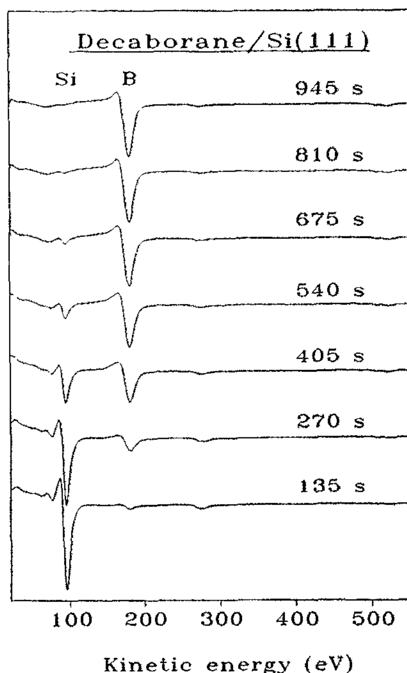

FIG. 1. Series of white light SR Auger electron spectra taken during exposure of a Si(111) substrate to 5×10^{-8} Torr decaborane and broadband synchrotron radiation. The total exposure time is indicated for each spectrum.

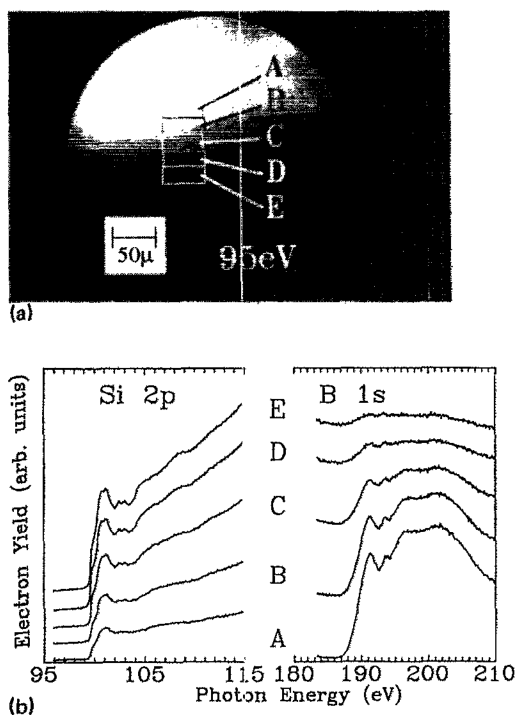

FIG. 2. (a) Photoelectron micrograph of the boundary region between a deposited boron film and the unexposed silicon substrate. The image was obtained at a photon energy of 95 eV, which emphasizes boron features. The letters A–E refer to the boxed areas in the image. (b) Series of NEXAFS spectra obtained in the areas labeled A–E in (a). The features in the spectra on the left are due to excitation of a Si 2*p* electron, while those on the right are due to excitation of a B 1*s* electron.

sorbed energy = 300 J), the Si signal has been completely attenuated and only the boron AES signal is evident. [Note the lack of signals attributable to carbon (272 eV) or oxygen (503 eV) which would be observed if the films had become contaminated during growth.] (There is a small carbon signal from the substrate, which is attenuated as the film grows.) To grow a 1 cm^2 film of the same thickness, at this pressure, under typical x-ray lithography conditions (0.4 W/cm^2) would take ~4 h, although the rate would increase substantially at higher pressures.

The initial rate of film growth may be estimated by the rate of attenuation of the Si AES peak at 92 eV. The mean free path of 92 eV electrons is ~5 Å.[13] After 6 min of exposure the Si AES signal had decreased by $1/e$ of its initial value. After correcting for the 48° take-off angle, we find an initial growth rate of ~1 Å/min. This rate was found to decrease with substrate temperature and increase with decaborane pressure, in agreement with previous models of SR-induced film growth.[3] Details of the temperature and pressure dependence of the film growth will be presented elsewhere.[14]

After film deposition the sample was transferred, in air, to another chamber where photoelectron microscopy,[15] coupled with near-edge x-ray absorption fine structure (NEXAFS) was used to study the pattern definition and chemical composition of the film. The micrograph shown in Fig. 2(a) was taken at the boundary region between the deposited film and the substrate. This image was obtained at 95 eV, a photon energy which emphasizes features due to boron. The boundary is sharp (~50 μm) relative to the area of the film (2×2.5 mm), which indicates that boron resulting from the dissociation of gas-phase molecules does not contribute to film growth.

In order to determine the chemical content in the boundary region, NEXAFS spectra were obtained for the areas denoted A–E in Fig. 2(a). Spectra were obtained for two energy regions: 95–115 eV (Si 2*p* excitation), and 180–210 eV (B 1*s* excitation), and are shown in Fig. 2(b). In going from the boron film to the unexposed silicon substrate, one observes a decrease in intensity of the boron-related features, while those due to silicon increase in intensity. The mean free path of the secondary electrons detected in this measurement is ~20 Å.[16] Based on the amount of time used to deposit this film (20 min), we estimate it's thickness to also be ~20 Å. Therefore, one would expect the Si-related features to decrease in intensity by $1/e$ (37%) in going from the Si substrate to the deposited film. The observed decrease of 33% is in reasonable agreement with this prediction.

Insight into the chemical structure of the boron film may be gained from the NEXAFS spectra in Fig. 2(b). The spectra in Fig. 2(b) are very similar to that of clean, polycrystalline boron,[16] but different from that of condensed decaborane.[17] The dissimilarity between the NEXAFS spectra of the SR CVD deposited film and that of condensed decaborane may indicate the lack of hydrogen in the former. The only significant difference between the clean boron NEXAFS and that of Fig. 2(b) is the presence of the small feature at 193.7 eV in the SR CVD film. This

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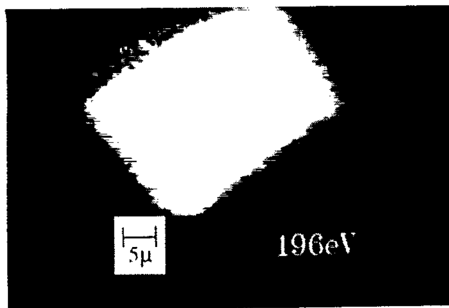

FIG. 3. Photoelectron micrograph of a region of a boron film deposited by using a 500 l/in. copper mesh as a mask. The image was obtained at a photon energy of 196 eV, which emphasizes boron features.

feature was found to have a greater intensity in films that were exposed to air for long periods of time. Therefore, we suggest it arises from excitation of a B 1s electron in a boron atom to which oxygen is bound as a result of air exposure. The fact that neither the Si 2p or B 1s NEXAFS spectra change appreciably through the boundary region may indicate a sharp interface with little Si-B chemical interaction. However, since the Si(111)-B($\sqrt{3} \times \sqrt{3}$)$R30°$ system also has a similar B 1s NEXAFS spectrum,[10] it is not possible to make this conclusion without further study.

In order to examine the potential of this technique for patterned deposition using masking techniques, we performed a deposition with a 500 ℓ/in. copper mesh in direct contact with or close proximity to the silicon substrate. A photoelectron micrograph of a region of the deposited film is shown in Fig. 3. The image was obtained at a photon energy of 196 eV, which emphasizes boron features. The edges of the image indicate an upper limit for the linewidth of $\sim 2\ \mu$m, which shows it is possible to obtain reasonably sharp patterns even using a crude masking technique. In related photoelectron spectroscopy measurements[17] we have found that by properly annealing SR-deposited boron films, it is possible to cause localized bulk diffusion, which indicates the potential of this technique for patterned, δ doping of semiconductors.

In conclusion, we have deposited contamination-free boron films on silicon at room temperature using decaborane as a source gas and broadband synchrotron radiation to excite the surface complex. The deposited films were localized to the region exposed to the radiation and the substrate temperature rose less than 10 °C, thereby indicating that gas phase and thermal processes are unimportant. Photoelectron microscopy NEXAFS measurements indicated that the films were relatively stable to oxidation by air. Masking techniques show promise for selective area deposition, which if coupled with x-ray lithographic methods and proper annealing, could be used for electronic device manufacturing.

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