ION AND ELECTRON BEAM PROCESSING OF CONDENSED MOLECULAR SOLIDS TO FORM THIN FILMS

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ABSTRACT

Electron and ion beams can be used to deposit thin films and etch surfaces using gas phase precursors. However, the generation of undesirable gas phase products and the diffusion of the reactive species beyond the region irradiated by the electron or ion beam can limit selectivity. In this paper, the feasibility of processing _condensed_ precursors such as diborane, tri-methyl aluminum, ammonia and water at 78 K with low energy (100-1000 eV) electron and ion beams (Ar^+, N_2^+ and H_2^+) ranging in current density from 50 nA to several μa per cm^2 is examined.   It was found that boron, boron nitride and stoichiometric aluminum oxide films could be deposited from the condensed volatile species using charged particle beams and some of the physical and chemical aspects and l'.nitations of this new technique are discussed.

INTRODUCTION

Ion and electron beam processing of materials plays an important role in the fabrication of microelectronics and increasingly these techniques are being used to make nanosized structures [1]. High flux charged particle beams can be focused to submicron dimensions and are often used to construct prototype devices whose size plays an important part in governing their physical properties.   Successful uses of ion beams in making micro structures include ion implantation and reactive ion etching.   Electron beams are used to fabricate masks and pattern thin films. Electron and ion beams can be used to deposit thin films. Some of the limitations of using charged particle beams to selectively deposit thin films on a microscopic scale are obvious.   The usual schemes for depositing thin films using ion beam or electron beam excitation of the gas phase precursors either coat the entire substrate (i.e. plasma assisted chemical vapor deposition (_p_-CVD)) or have a limited ability for making micro structures because the reactive chemical species can drift out of the energetic beam used to activate the gaseous precursors.

An alternative to gas phase precursors are solid precursors that can be converted to the desired product by 1) electron, 2) inert ion or 3) reactive ion bombardment and successful fabrication of micro structures has been demonstrated for all of these techniques [2]. One drawback of this approach is the fact that the non-converted precursor material remains on the substrate and either has to be suitable for another use in the structure (e.g. an insulator) or readily removed from the substrate. Such materials could be made volatile and some temperature and be removed from the substrate by heating to that temperature. Gases often used in microelectronics fabrication can be condensed on sufficiently cold substrates (e.g.

SiH_4 at 60 K) and when activated by non-thermal means should in theory react to form useful inorganic coatings like silica or α-Si.

This paper describes an examination of the feasibility of using low energy ion or electron beams to process molecular solids at cryogenic temperatures to make useful coatings. Electron and Ar^+ beams were used to convert condensed diborane (B_2H_6) to a hydrogen-rich or boron film and N_2^+ beams were used to convert condensed diborane to boron nitride. The work shows that condensed gases can be non-thermally activated and processed into the solid phase or that energetic ions can be used as reactants to convert molecular films into solids at extremely low temperatures.

EXPERIMENTAL DETAILS

The experiments were conducted in an ion and turbopumped vacuum system capable of reaching the 10^{-10} Torr range after vacuum bake out. Standard surface analytical tools for x-ray photoelectron spectroscopy (XPS) were available for analysis of the substrates and thin films at each stage of their processing. The electron beam source was the ionizer of a quadrupole mass spectrometer (UTI-100C) which was biased to extract the electron beam. The sample was a silver foil which was attached to a copper cold finger using stycast epoxy. The entire cold finger and cryostat were isolated from the vacuum chamber using a ceramic vacuum break. The sample could be biased from 0-1000 V and this was used to vary the incident particle energy and focus the charged particle beam on the substrate. A sputter ion source operated at low energy was used to generate argon, nitrogen or hydrogen beams. When the samples were bombarded using ions, they were biased at - 250 V. This was done not only to control the energy of the incident beam but to also repel electrons or negatively charged particles from striking the surface. Hence, we attribute the ion processing results to the positively charged species.

The cold finger was cooled to liquid nitrogen temperature (~ 80 K) and the silver foil sputtered with an Ar^+ beam to provide a clean surface. The absence of impurities was verified by XPS scans of the energy ranges where the 1s core levels of such impurities as C,N and O are found. Next, the surfaces were coated with diborane which was condensed from a commercial 5% B_2H_6 / 95% Ar mixture. Lower temperatures than 80 K are needed to condense argon at these pressures, so the diborane films condensed were pure. Typical times required to condense several monolayers of diborane were 400 s with a combined diborane/Ar partial pressure of 5 x 10^{-5} Torr. The estimated diborane exposure was 10^4 L (1 L = 10^6 Torr-sec). After the diborane was administered to the surface, the vacuum chamber was pumped down and the B_2H_6 was irradiated with electrons or ions. At selected intervals the electron or ion bombardment was stopped and XPS scans done to study the electronic or compositional changes in the molecular solid. After substantial changes to the composition or electronic properties of the molecular layer, the liquid nitrogen was removed from the cryostat and the sample was allowed to warm up to a point where diborane should be thermally removed from the surface. As the data shows, the irradiation of condensed diborane films by energetic electrons or ions produces thermally stable films whose XPS spectra resemble boron or boron nitride coatings.

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RESULTS AND DISCUSSION

Figure 1 shows the modification of the boron 1s core level for electron processing of a B_2H_6 film to make either a boron or a boron hydride coating which is not volatile at room temperature. The initial position of the boron 1s core level is at a binding energy of - 190.5 eV and the width of the core level is several electron volts. Even with our modest resolution, it is apparent that the diborane interacts with the silver support and the resulting layer has several in equivalent local environments. When the film was allowed to warm up the molecular film desorbed from the surface between 100-110 K and the RGA cracking pattern was identical to diborane.

Electron irradiation caused the B 1s peak to shift to -188 eV binding energy. The sample was bombarded by 100 eV electrons for 400 s. and the electron current was 0.4 μA. Solid boron has a binding energy of -188 eV and it could be concluded that electron bombardment causes the fragmentation of diborane and the removal of hydrogen which in its molecular form is volatile at 80 K. To determine whether diborane had been converted to elemental boron or a non-volatile boron hydride (e.g. decaborane), the sample was warmed to 150 K. The B 1s peak moved a few tenths of an eV to higher binding energy and decreased approximately 10-15 % in intensity. A reference B_2H_6 film, not subjected to electron bombardment, was almost completely removed from the substrate at this temperature.

At this point we can only speculate about the physical mechanisms at work during the electron bombardment of the diborane. At a kinetic energy of 100 eV the electrons greatly exceed the typical
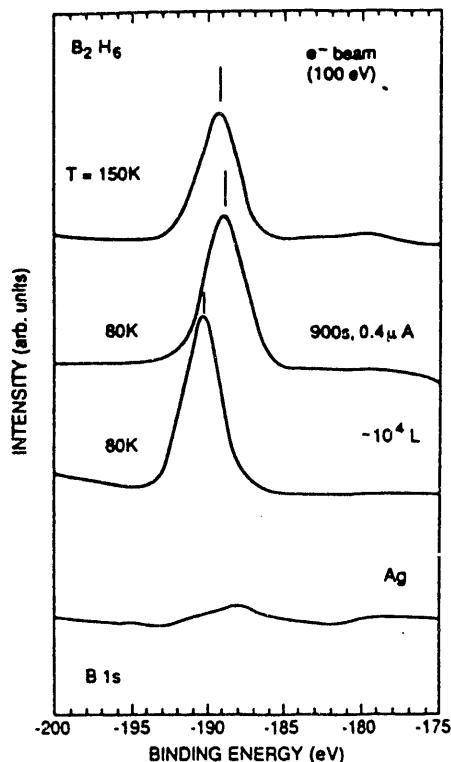

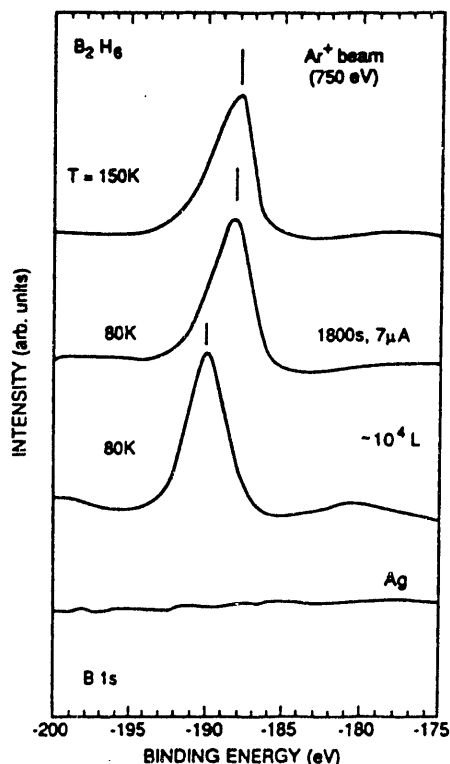Figure 1. Conversion of condensed B_2H_6 to a boron or boron hydride by a low energy electron beam.

Figure 2. Conversion of solid B_2H_6 to a boron or boron hydride by a low energy argon ion beam.

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thresholds for electron attachment or fragmentation of diborane by electrons [3]. An alternative means of activation of diborane in a condensed solid is bombardment by rare gas ions [4]. Such charged particles could exchange energy with the B_2H_6 molecules by collisions [5]. Rare gases have very high partial pressures at 80 K and are chemically inert. Hence, they should be easy to remove from thin surface layers.

Figure 2 shows the results obtained for bombarding a B_2H_6 film with 750 eV Ar^+ ions. As previously mentioned the Ar^+ source generated a 500 eV beam which was accelerated by a 250. V bias toward the sample. The same bias also repelled electrons produced by the Ar^+ source. The processing parameters were 1800s exposure time and an ion current of 7 μA. A similar boron film was produced and the amount of boron sputtered from the surface was small. Ion beam processing of molecular solids is limited by the small cohesive energy of most molecular solids which leads to sputtering when the ion energy exceeds a specific threshold. When the energy is low enough to avoid sputtering another concern is the amount of energy or momentum transferred to the molecular precursors by the incident ions. If the energy and momentum transfer are too small to get over the reaction activation barrier the ions will ricochet off the molecules and do nothing [6].

Incident ion beams can also act as a source of one of the reactants. Such a reactant would be very reactive and carry into the reaction the energy need to thermally activate the reaction [7]. It is possible, even at low ion energies to exceed the typical activation energies of chemical processes by at least an order of magnitude, so it may not only be possible to make
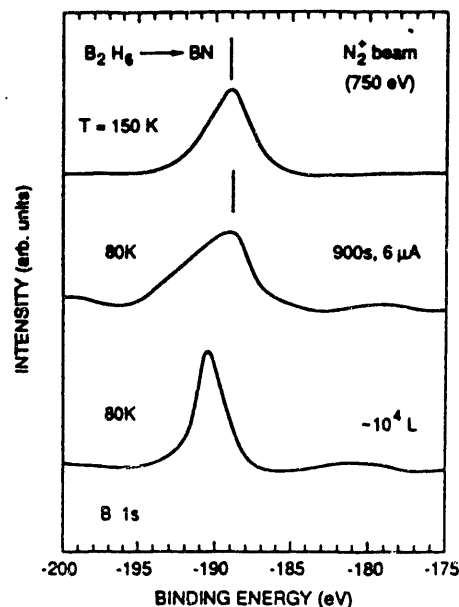
Figure 3. B 1s spectra for the reaction of a nitrogen ion beam with diborane to form boron nitride.
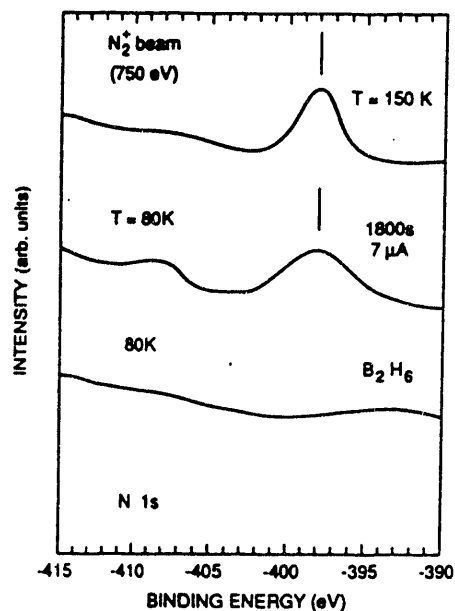
Figure 4. N 1s spectra for the reaction of a nitrogen ion beam with diborane to form boron nitride.

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ordinary chemical compounds but also make new materials with different structures and properties. In the example described in figures 3 and 4, we demonstrate that a energetic N_2^+ beam can be reacted with diborane to make a thin film that resembles boron nitride. It should be emphasized that BN is representative of a class of hard materials like diamond that are normally produced using energetic species normally created in a plasma or synthesized under extreme thermal conditions. Figure 3 shows how the B 1s core level is modified when condensed diborane is bombarded using nitrogen ions. The nitrogen ion processing lasted 900 s. and the incident ion current was 6 μA. The B 1s core level broadens and develops a pronounced asymmetry oriented towards lower binding energy. This is interpreted as the growth of another B 1s core level component at lower binding energy due to the formation of a new boron containing phase. An examination of the film for nitrogen finds that some nitrogen is retained in the diborane layer. The N 1s peak is initially centered at -398 eV binding energy and is relatively broad suggesting a series of nitrogen bonding configurations rather than a single B-N configuration. From the binding energy of the N 1s peak it is clear that the nitrogen has not reverted to molecular nitrogen and may have formed a nitride. At this point the nitrogen bombardment of the diborane film was halted and the nitrogen containing diborane film was heated to remove the un-reacted diborane and other volatile components. This procedure changed the B 1s peak and sharpened the N 1s line. The B 1s core level becomes much more symmetric and the resulting peak which resembles a Gaussian function is found at - 189 eV binding energy. Typical values for BN range from - 190 to - 190.5 eV [8]. However, B 1s binding energies as low as - 189 eV reported by other workers [9] and thin BN films showing the characteristic N and B k-edges of boron nitride have the same binding energy [10]. The same considerations apply to the binding energy of the N 1s peak. It is still centered at - 398 eV binding energy and has about the same width as the B 1s peak. The resulting film is non-volatile at 150 K and higher temperatures and this along with the photoelectron data makes a case for the formation of a thin BN layer.

Other systems were tried with varying degrees of success. In related work by our group using photon beams to activate reactions with condensed molecular films, alumina and silicon films were deposited using precursors like diborane and ammonia to make BN [10], tri-methyl aluminum (TMA) and water to make Al_2O_3 [11] and tetra-methyl silane and ammonia or water to make silicon or SiO_2, respectively [12]. To determine whether charged particles could drive reactions in mixtures of molecular solids at low temperatures, an Ar^+ beam was directed into a TMA/H_2O mixture at 80 K. We found that TMA and water interact at 80 K but form a compound which is volatile and contains significant amounts of carbon. In work using photon beams, a reaction liberating virtually all of the carbon as methane or CO and forming an aluminum oxide or related phase containing some hydrogen or hydroxyl was activated by the photon beam. When a 6 μA 750 eV Ar^+ beam was directed into the TMA/H_2O mixture for 1800 s., XPS spectra showed evidence that the aluminum was converted to Al_2O_3 and some of the carbon was liberated from the film. The thickness of the film was reduced by sputtering and the loss of some material via the formation of methane or CO. The aluminum oxide produced by this technique was

thermally stable and remained on the surface after all of the volatile precursors and produces were removed from the surface by heating to 150 K.

CONCLUSIONS

Electron, rare gas ion and nitrogen ion beams were used to process condensed diborane, into boron or boron nitride films. The volatile nature of the precursors facilitates the formation of small structures when focused charge particle beams are used to pattern the films because the films are selectively deposited only when activated by the charged particle beam. The unreacted material can be removed by allowing the sample to return to 300 K. Other potential advantages of this processing technique include the great reduction in the amounts of the precursor chemicals needed for processing and the elimination of activated precursors that can drift out of the charged particle beam. Other obvious advantages are related to the transport and elimination of the scattering of the charged particle beam when directed into a gas. This work is at an early stage and much remains to be done to establish the technique as a usable process for materials fabrication.

ACKNOWLEDGMENTS

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