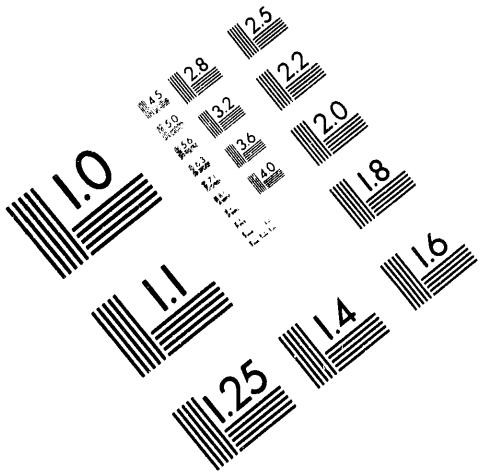

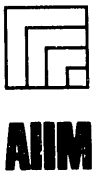

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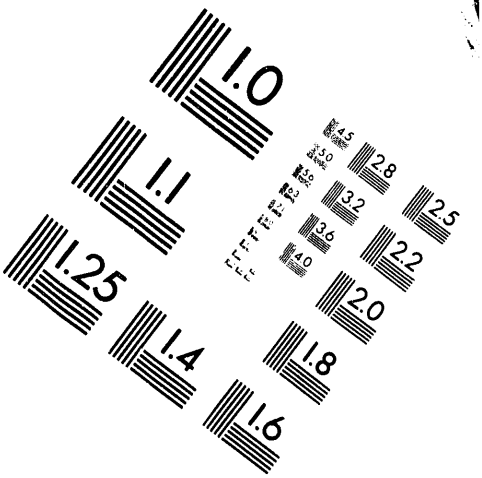

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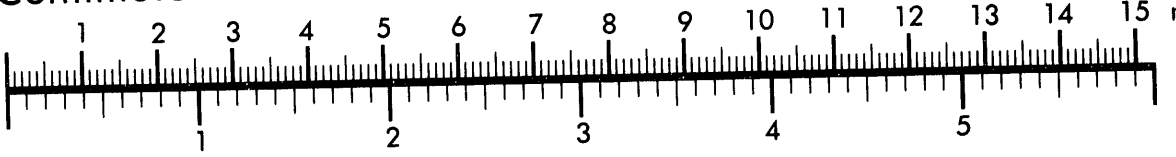

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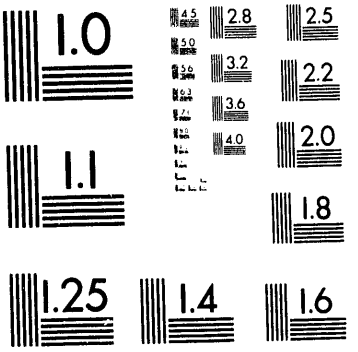

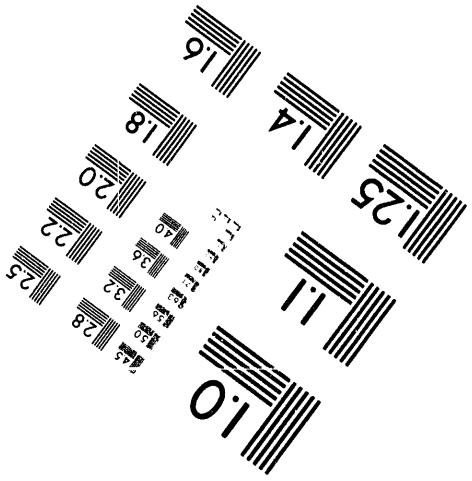

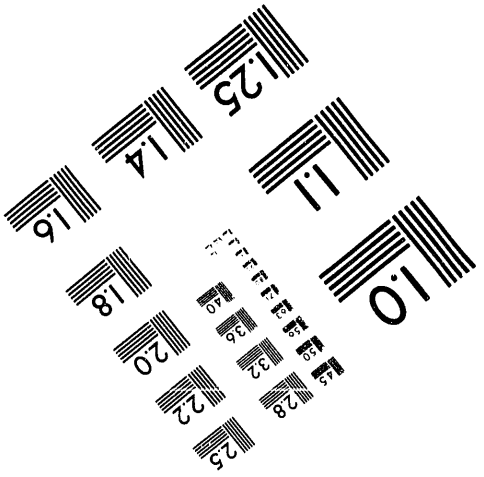

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GROWTH OF DIELECTRIC THIN FILMS BY IRRADIATION OF CONDENSED MOLECULAR PRECURSORS WITH SYNCHROTRON RADIATION

BNL-48420

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ABSTRACT

Spectroscopic evidence is presented that shows that boron nitride and aluminum oxide can be synthesized by exposing a condensed layer of molecular precursors to synchrotron radiation. In the Al_2O_3 circumstance a condensed layer of trimethylaluminum (TMA) and water at 78 K on a silver substrate produces pure layers of aluminum oxide. Using the same condensed layer technique boron nitride is produced by exposing a solid matrix of diborane and ammonia to synchrotron radiation. Near edge x-ray absorption fine structure and core level photoelectron spectroscopies are used to characterize the Al_2O_3 and BN layers, which were typically 30Å thick. During the formation of aluminum oxide the carbon component in the alkylaluminum precursor is completely removed during irradiation as a volatile methane product which was detected by mass spectrometry. In the absence of synchrotron radiation the molecular precursors in both the aluminum oxide and boron nitride systems show evidence of some interactions within the solid, but upon warming to near room temperature (260 K) the layers desorb from the substrate.

INTRODUCTION

The synthesis of dielectric thin films from gaseous precursors by a photon assisted technique has many potential applications in the microelectronics industry and in the area of insulating or hard coatings. We show in this paper that two such materials, aluminum oxide (Al_2O_3) and boron nitride (BN), can be synthesized from a condensed (78 K) layer of trimethylaluminum (TMA) - water and diborane - ammonia, respectively, in the presence of synchrotron radiation.[1,2] The use of synchrotron radiation to assist the growth of thin films is not new and has already been addressed by various researchers.[3,4,5] We present, however, a novel technique that irradiates intimately mixed condensed molecular precursors with synchrotron radiation to synthesize thin films.

Using a *condensed* layer as the reaction matrix offers several advantages over other higher temperature deposition techniques. First, a layer of reactants can be condensed, typically 50 - 100 Å, so that a high density of reactant molecules can be achieved, even in the ultra-high vacuum environment where the vapor pressure of the layer must be below 10^{-8} Torr. After exposure any unreacted material is removed by simply warming the sample to ambient temperatures. Second, the relative ratios of the reactants can be varied to achieve the desired thin film stoichiometry. Third, the film growth occurs on the substrate surface, opposed to gaseous reactants, so that epitaxial growth may be possible in some systems. Finally, since the deposition is performed in the ultra-high vacuum environment a variety of surface science techniques can be used to characterize the film before, during, and after synchrotron irradiation.

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EXPERIMENTAL

The research presented in this letter was carried out on the U7A beamline at the National Synchrotron Light Source (NSLS). The experimental ultra-high vacuum (UHV) chamber was pumped by both ion and turbomolecular pumps, and had a typical base pressure during irradiation of about $2x10^{-9}$ Torr. The substrate was prepared by evaporating silver onto the copper surface of a cryostat which was held at 78 K with liquid nitrogen. The silver substrate was considered clean when contaminants such as oxygen and carbon were below the detection limit of photoemission. The near edge x-ray absorption fine structure (NEXAFS) measurements were performed in the total electron yield mode and all of the NEXAFS data in this letter have been divided by a spectrum obtained from the clean silver substrate, to account for the behavior of the monochromator. All of the core level data was taken with a Vacuum Science Workshop hemispherical analyzer (44 eV pass energy). The C(1s) and Al(2p) binding energies (referenced to E_F of silver) were obtained by using photon energies of 400 and 200 eV respectively.

Diborane (B_2H_6), ammonia, TMA ($(CH_3)_3Al$), and H_2O were introduced into the UHV chamber through 1/8" stainless steel dosing tubes. Typical dosing pressures were about 10^{-7} Torr as measured by a uncorrected ionization gauge. Effective pressures at the sample were estimated to be at least an order of magnitude higher due to the line-of-sight dosing configuration. The TMA (or diborane) and H_2O (or ammonia) dosing tubes were 180° apart, and hence the sample was cycled between each doser during preparation of the condensed layers. This procedure was used to ensure the best possible mixing, under our conditions, between the reactants. The purity of all reactants was checked prior to use by mass spectrometry. The condensed precursors, for the experiments presented here, made about a 50Å thick film and the relative concentration of B_2H_6 to NH_3 was about 1:1 and that of H_2O to TMA was about 3:1. All irradiations of the *ice* layers were done with *zero*

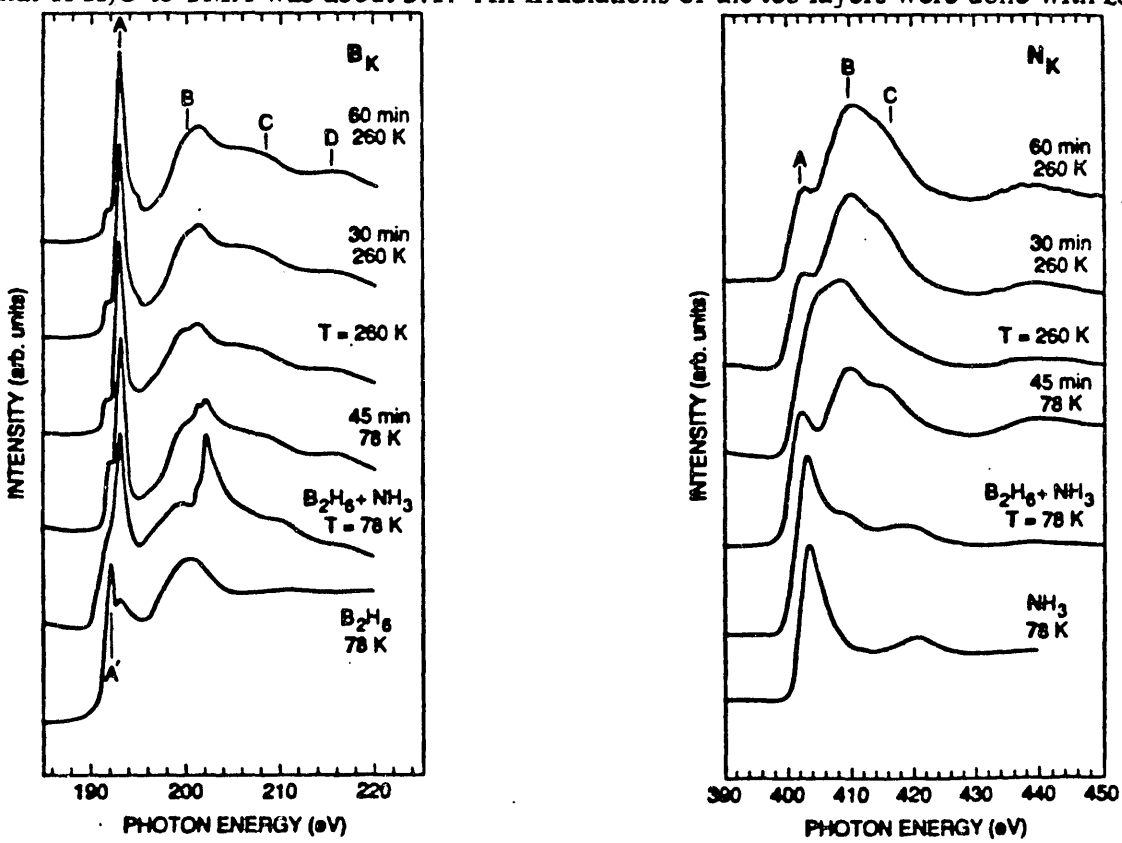

Figure 1 a) Boron K-edge measurements for solid diborane, diborane - ammonia mixtures before and after irradiation; b) nitrogen K-edge measurements for the same experimental conditions.

RESULTS

Boron nitride

Figure 1a exhibits boron NEXAFS on pure condensed diborane and on diborane/ammonia mixtures (78 K) before and after irradiation and thermal treatment to room temperature. It is readily apparent that by co-condensing ammonia with diborane there are noticeable changes in the diborane molecule. Peak A' , associated with transitions of the B-1s core electron to unoccupied valence levels in the diborane molecule decreases and a new feature appears about 0.75 eV to higher photon energy when ammonia is present. The result suggests that even at 78 K there is an interaction between the diborane and ammonia molecules. Warming the sample to room temperature recovers the clean silver surface suggesting that this diborane - ammonia interaction is easily broken or that the adduct (possibly $(NH_3)_2BH_2BH_4$[6]) is volatile. It should be mentioned that the strong feature at about 200 eV which appears when ammonia is present is a second-order N K-edge spectrum of nitrogen in ammonia and is shown to appear at 400 eV in first order in Figure 1b. The N-edge also shows the diborane-ammonia interaction in the second from the bottom spectrum. The feature found at 420 eV in pure ammonia is shifted to lower photon energy when diborane is present and a new feature appears at 410 eV.

Exposure of the diborane/ammonia condensed layer to synchrotron radiation for 45 minutes at 78 K produces hydrogen product as evidenced by mass spectrometry. Significant changes in both the B-1s and N-1s NEXAFS spectra also occur as shown in the third from the bottom spectra in figures 1a and b. The most revealing features to appear after irradiation are the 200, 208, and 216 eV features in the B-NEXAFS and the 403, 410, 416, and 440 eV features in the N-NEXAFS spectrum. The features are in excellent agreement with those reported in the literature for hexagonal BN.[7]

Thermal treatment of the sample to 260 K removes unreacted diborane and ammonia or any volatile reaction products. The N-NEXAFS also shows a broadening of the BN

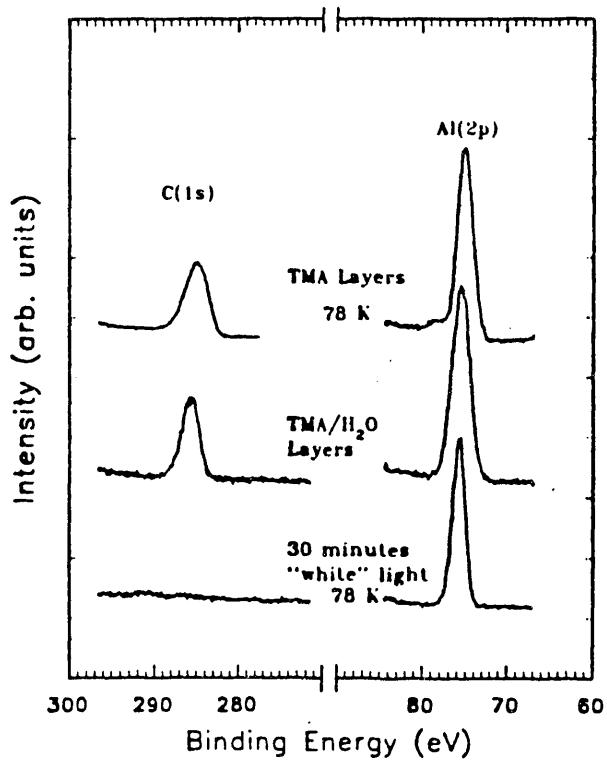

Figure 2: XPS measurements of a pure TMA condensed layer, TMA/H_2O mixture, and layer after synchrotron irradiation.

features possibly indicating some disordering of the film. Further irradiation of the film for 30 and then 60 minutes sharpen up the BN features so that peaks A, B, C, and D are again in excellent agreement in both relative intensity and energy position to bulk boron nitride.

Aluminum oxide

Figure 2 shows photoelectron spectroscopy measurements of the Al(2p) and C(1s) levels from condensed layers of TMA, TMA/H_2O mixtures, and after exposure of the ice mixture to synchrotron radiation for 30 minutes with subsequent warming to 260 K. The Al(2p) and C(1s) binding energies for condensed TMA layers are 75.0 and 285.0 eV, respectively, which is in excellent agreement with past photoemission studies on TMA.[8] In the condensed TMA/H_2O solid the Al(2p) peak is shifted to 75.5 eV and the carbon feature now appears at 285.5, suggesting that there may be some interaction between the TMA and H_2O at 78 K. An alternate explanation for this peak shift is charging due to the thickness of the film, which can't be ruled out at the present time. Warming the sample to temperatures above about 200 K removes the condensed layer as evidenced by the presence of silver (fully suppressed when the condensed layer is present) and the absence of carbon, oxygen, and aluminum in photoelectron measurements. This result confirms that thin film formation only occurs under our experimental conditions if the *ice* is exposed to synchrotron radiation.

After synchrotron irradiation of the TMA/H_2O ice at 78 K, the carbon is removed and the Al(2p) binding energy shifts slightly to 75.6 eV, which is in agreement with the Al(2p) binding energy for bulk aluminum oxide (Al_2O_3).[9] Using the attenuation of the underlying Ag(3d) photoelectrons (relative to the clean silver surface) as a gauge, the aluminum oxide layer is estimated to be between 20 and 30Å.

Figure 3 exhibits the oxygen K-edge NEXAFS spectra for TMA/H_2O layers, exposed

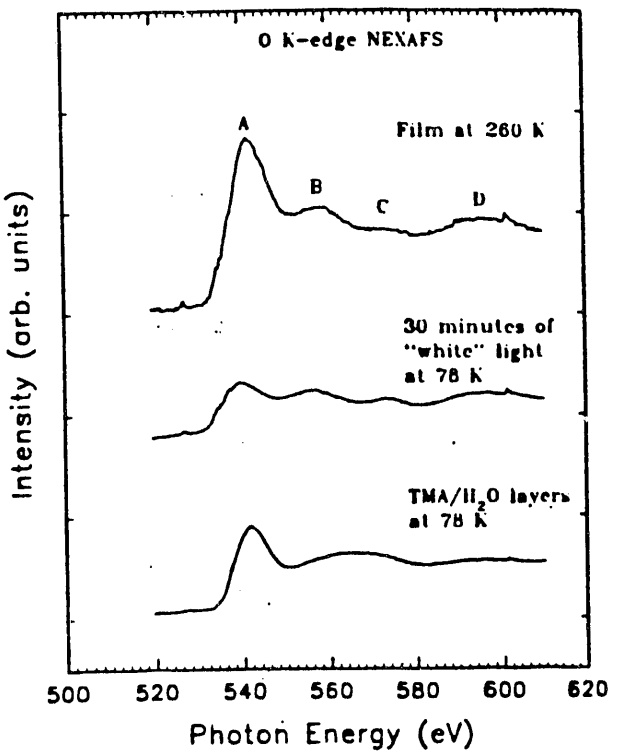

Figure 3: O-K edge NEXAFS spectra. Conditions are indicated in the figure. Peaks A, B, C, and D indicate that the thin film is stoichiometric Al_2O_3.

layers at 78 K, and the thin film at 260 K after irradiation. After a 30 minute irradiation at 78 K the NEXAFS spectra shows that significant reaction has occurred in the TMA/H_2O layers. Warming to 260 K leaves well defined oxygen near-edge features, denoted by *A*, *B*, *C*, and *D*. These peaks agree well with those features of bulk aluminum oxide[10], in both energy position and relative intensity. It should be stressed that our thin film electronic structure is consistent with stoichiometric Al_2O_3, since NEXAFS shows clear differences between bulk aluminum oxide and chemisorbed oxygen on aluminum.[7] This NEXAFS result also suggests that the condensed layers technique allows intimate mixing between the reactants in the TMA/H_2O system and hence, an uniform stoichiometry throughout the thin film can be obtained.

An interesting feature about the aluminum oxide result is that the surface carbon concentration is reduced to the undetectable limit by synchrotron irradiation. To determine the chemical form in which the carbon leaves the reaction zone, the *neutral* desorbing species in the m/e 1 to 60 range were monitored by electron impact mass spectrometry during irradiation of the TMA/H_2O adlayers. Methane was found to be the dominant desorbing product at 78 K (confirmed by the ratio of the m/e 15 (CH_3^+) to 16 (CH_4^+) ion cracking fragment peak). Carbon monoxide (m/e 28) and carbon dioxide (m/e 44) also were present during irradiation, but their yield was barely above our detection limit. Methane formation was initiated at the onset of irradiation and within two minutes of irradiation the methane product was reduced to a steady state value (about 1/10 of the maximum value) for the remaining irradiation time. The result suggests that the majority of the reaction was completed within a few minutes after exposure to the radiation. We have not performed a detailed study on the time dependence of the aluminum oxide formation, but we have found that after irradiation of the TMA/H_2O ice for 10 minutes that the Al(2p) core level and O-1s NEXAFS measurements are consistent with aluminum oxide formation. Carbon contamination, however, is present after these short irradiation times, suggesting that longer irradiation times are required to remove all the carbon in the film.

SUMMARY

Boron nitride and aluminum oxide have been synthesized by exposing intimately mixed condensed layers of B_2H_6/NH_3 and TMA/H_2O to synchrotron radiation at 78 K on a silver substrate. NEXAFS and XPS have been used to characterize the structure of the ~30 Å thin films. During BN formation at 78 K the dominant gaseous product is hydrogen while in the case of aluminum oxide, methane is the desorbing species.

ACKNOWLEDGMENTS

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