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SOME PROPERTIES OF RF SPUTTERED HAFNIUM NITRIDE COATINGS

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ABSTRACT

Hafnium nitride coatings have been deposited by reactive RF sputtering from a hafnium target in nitrogen and argon gas mixtures. The rate of deposition, composition, electrical resistivity and complex index of refraction have been investigated as a function of target-substrate distance and the fraction nitrogen, (f_{N_2}) in the sputtering atmosphere. It was found that the relative composition of the coatings is independent of f_{N_2} for values above 0.1. The electrical resistivity of the hafnium nitride films changes over 8 orders of magnitude when f_{N_2} changes from 0.10 to 0.85. The index of refraction is almost constant at 2.8 (1 - 0.3i) up to f_{N_2} = 0.40 then decreases to 2.1 (1 - 0.01i) for higher values of f_{N_2}.

INTRODUCTION

There has been a developing interest in the properties of and sythesis techniques for thin films of the group IV nitrides. These materials are characterized by high hardness and chemical stability and are finding increasing application in technology, appearing as barrier coating in the electronics industry[1] decorative coating for watch cases[2] and as wear reducing surface coatings for cutting tools[3,4]. At this laboratory, in pursuit of our interest in the tribological properties of promising materials we have begun a study of the characteristics of hafnium nitride films produced by reactive RF sputtering. This method does not, in con-

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trast to CVD techniques, require high substrate temperatures and therefore coatings can be applied to metals and other materials without degrading their bulk properties. The present study investigates some optical, electrical, and compositional properties of reactively sputtered hafnium nitride films and their dependence on sputtering conditions.

EXPERIMENTAL TECHNIQUE AND PROCEEDURE

The RF sputtering system used in this study was a commercial diode apparatus operated at 13.56 MHz and at a power density of 2.7 watts/cm^2. The target was high purity hafnium metal 15.2 cm in diameter and was water cooled. The sputtering chamber was a pyrex bell jar which was diffusion pumped and liquid nitrogen baffled. The system base pressure was $<2 \times 10^{-6}$ torr. The sputter gases, nitrogen and argon, were leaked continuously at about 200 scc/m into the system. An orifice between the bell jar and the pumping system was used to allow the diffusion pump to operate on the plateau of its pumping speed curve. The total gas pressure, typically 20×10^{-3} torr, was regulated with a commercial piezoelectric leak valve and controller system. The composition of the sputtering atmosphere before and after the deposition was monitored with a differentially pumped mass spectrometer. At each pump down 3 sample sets were run. Each set consisted of 9 samples: 3 each of silicon, quartz and 304 stainless steel. One of each substrate was located at each of the 3 substrate to target distances (25 mm, 37 mm, 50 mm). The sputtering times varied from 3 to 15 minutes. The fraction of nitrogen (f_{N_2}) in the sputtering atmosphere was varied from 0.1 to 0.85. The quartz sample was masked so as to deposit a strip 3 mm wide and 20 mm long for resistance and thickness measurements. The thickness of the films, 40 – 200 mm, was measured with a commercial stylus profilometer. Surface roughness limited the thickness measurement accuracy to ±20 nm. For

electrical resistivity measurements gold contacts were sputter deposited at the ends of the quartz samples. The DC resistivity was determined by applying a voltage (0.5 to 10 V) and measuring the current with a digital electrometer. All samples were found to be ohmic. The complex index of refraction $\hat{n}$ (= $n(1 - ik)$) was measured by ellipsometry at a wavelength of 632.8 nm. The data was reduced using the computer program developed by McCracken[5]. Due to the limited accuracy of the thickness measurements, unambiguous results for n and k were not usually possible. Therefore, the computed optical parameters for the films on the three different substrates were combined, under the assumption that all were identical optically, to give the results quoted. Composition measurements were made by Auger Electron Spectroscopy (AES) of the films on 304 stainless steel. A conventional single pass cylindrical mirror analyzer with an integral electron gun was used. The electron beam was operated at 2 kV and 2 μA. The data was taken in the dN/dE mode using a modulation amplitude of ±1 volt. The samples were sputter cleaned with 3 kV argon ions until a constant spectrum was obtained. AES data was always taken while sputter cleaning to minimize the amplitude of both carbon and oxygen peaks. Typical base pressure of the AES vacuum system was $<2 \times 10^{-10}$ torr. AES measurements were made with the system backfilled with high purity argon to a pressure of 3×10^{-5} torr.

RESULTS

It was found that the deposition rate was independent of the substrate material, however, it did depend strongly on both f_{N_2} and the substrate to target distance. In figure 1 is shown the deposition rate as a function of f_{N_2} for the three different substrate to target distances. For the entire range of f_{N_2} studied (0.1 to 0.85) the rate of deposition decreased as f_{N_2}

increased. This is consistent with earlier observations[6] which showed that sputter rates in pure N_2 are typically 1/2 of the sputter rate in pure argon. A linear dependence of the sputter rate on the substrate to target distances was also observed with the sputter rate increasing as the substrate to target distance decreased. Approximately a 30-percent increase in sputter rate is observed when the distance is decreased from 50 to 25 mm.

The AES spectra contained only hafnium, nitrogen oxygen and carbon peaks. In figure 2 the ratios of the nitrogen, carbon and oxygen KLL peak heights $(I_x$, x = N,C,O) to the hafnium (185V) peak height (I_{Hf}) are plotted as a function of f_{N_2}. All three ratios are seen to depend weakly on f_{N_2} demonstrating that the films' composition, as seen by AES, does not depend strongly on the partial pressure of nitrogen in the sputter gas. Converting these ratios to absolute compositions requires either a standard sample or reliable sensitivity factors and a quantitative understanding of preferential sputtering in the $HfN_xC_yO_z$ system. Since neither was available we use published sensitivity[7] factors and assume that, with respect to preferential sputtering HfN behaves qualitatively the same as TiN. In that system both nitrogen and oxygen are known[8] to sputter preferentialy with respect to titanium and carbon. Further it has been found[8] that carbon can appear as an artifact in AES measurements due to the reduction of methane at the surface by both the sputtering ions and the electron beam. The methane background increases in ion pumped vacuum systems when, in order to sputter clean the sample, the ion pump is turned off. To quantify the carbon artifact a sample of high purity hafnium metal was studied. Its AES spectrum gave I_c/I_{Hf} = 0.34 and I_o/I_{Hf} = 0.095. The ratios in figure 2 combined with the above considerations implies that the film's composition is $HfN_xO_yC_z$ where x > 0.7, y > 0.01, and z < 0.08.

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Figure 3 is a semi-logarithmic plot of DC resistivity as a function of f_{N_2}. At low values of f_{N_2} the films have near metallic conductivity ($\sim 10^{-2}\Omega$cm) while at the highest values of f_{N_2} it reaches $\sim 10^6\Omega$cm, a span of 8 orders of magnitude. This strong dependence on f_{N_2} is in sharp contrast to the behavior of the composition. The resistivity also shows a systematic dependence on the substrate to target distance being larger for larger distances for a given f_{N_2}. The resistivity found here though significantly higher ($\sim \times 10^3$) than those reported by Smith[9] for DC sputtered films, does vary similarly with increasing nitrogen partial pressure in the sputtering gas.

The ellipsometer data is presented in figure 4 where n and k are plotted as functions of f_{N_2}. Both are seen to be independent of f_{N_2} for $0.1 < f_{N_2} < 0.4$ where $n = 2.8\pm0.1$ and $k = 0.03\pm0.1$. Above 0.4 both indices decrease significantly with k approaching zero and n 2.1 at $f_{N_2} = 0.8$. This behavior may signal a phase change as reported by Smith[9] who observed a change in structure at approximately the nitrogen partial pressure corresponding to $f_{N_2} = 0.4$.

The hafnium nitride films deposited on 304 AISI stainless steel substrates exhibited bright colors over the whole visable spectrum. The observed colors are typical of dielectric films on strongly absorbing polished substrates. Calculated reflectivity curves based on the experimental values of the index of refraction, absorption and film thickness were in good agreement with the observed colors over the entire range of deposition conditions.

CONCLUSIONS

A series of hafnium nitride films were produced by reactive RF sputtering of a pure hafnium metal target over a range of sputtering gas mixtures. Measurements of the films' properties reveal:

(1) The films' composition is approximately independent of the fraction (f_{N_2}) of nitrogen in the sputter gas for $0.1 < f_{N_2} < 0.85$.

(2) The deposition rate is maximized at low values of f_{N_2} and small substrate to target distances.

(3) The DC resistivity increases strongly with increasing f_{N_2}. If the band structure and electronic properties are as reported then the films with low values of f_{N_2} have the smallest defect concentrations.

(4) A possible phase change at $f_{N_2} \sim 0.4$ is indicated by a change in the index of refraction from 2.8 to 2.1.

REFERENCES

1. M. Sekinoto, H. Yoshihara, T. Ohkubo, and Y. Saitoh, Jpn. J. Appl. Phys., 20, L669 (1981).

2. T. Tomita, I. Kasai, and T. Koshiki, Japan Pat #a7630525 (1971).

3. Roy V. Leverenz, Manuf. Eng. 79 (1) 38-39 (1977).

4. M. Kodama, A. W. Shabalk, and R. F. Bunshah, Thin Solid Films 54 (1978) 353-357.

5. F. L. McCrackin, Nat. Bur. Stand. (U.S.) Tech. Note 479, Apr. 1978.

6. J. L. Vossen and W. Kern, Thin Film Processes (Academic Press, New York, 1978), p. 17.

7. P. W. Palmberg, G. E. Raich, R. E. Weber, and N. C. MacDonald, Handbook of Auger Electron Spectroscopy (Physical Electronics Industries Inc., Eden Prairie, Minn., 1972).

8. S. Ingrey, M. Johnson, and R. W. Streeter, AVS 28th National Symposium Proceedings Abstracts, (1981), p. 48.

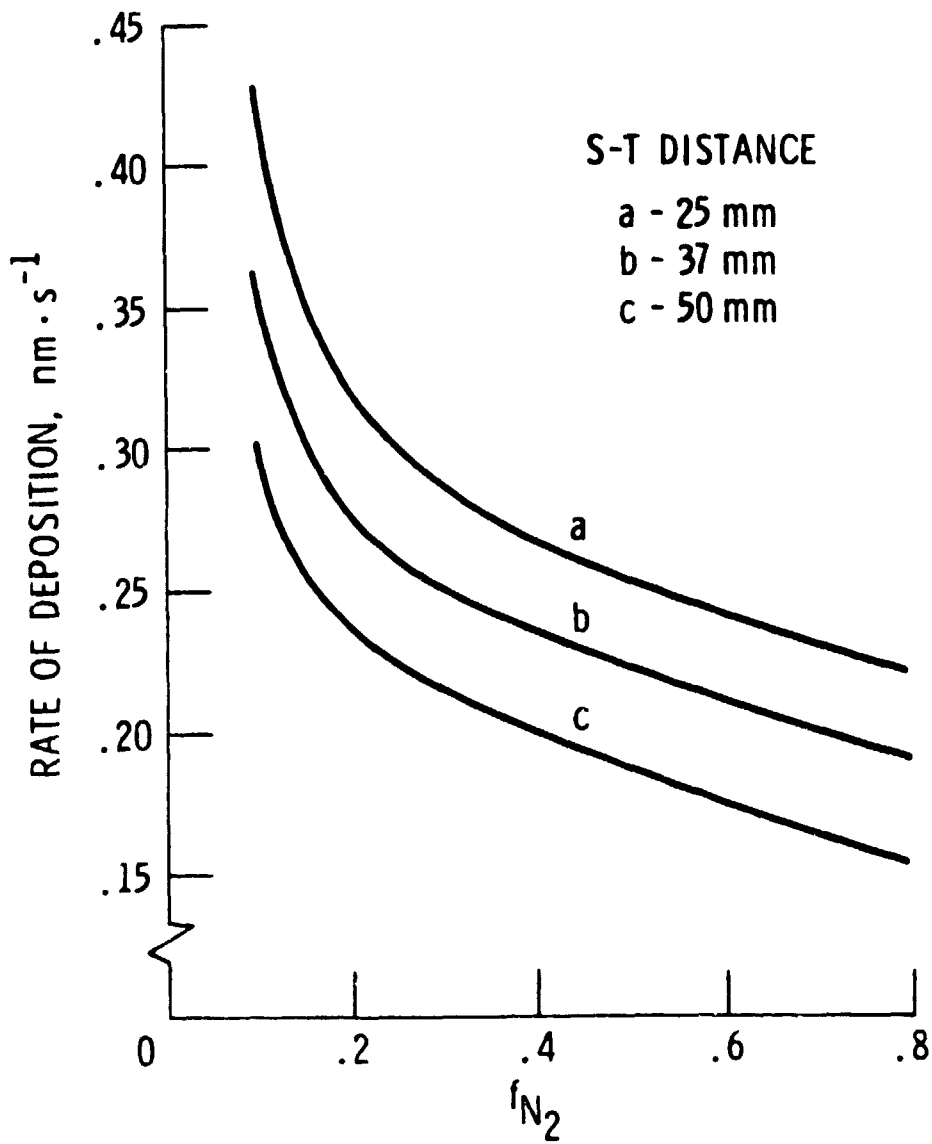9. F. T. J. Smith, Jap 41 (10) 4227-4231 (1980).

Figure 1. – Deposition rate as a function of f_{N_2} at 23 m torr for 3 substrates to target distances.
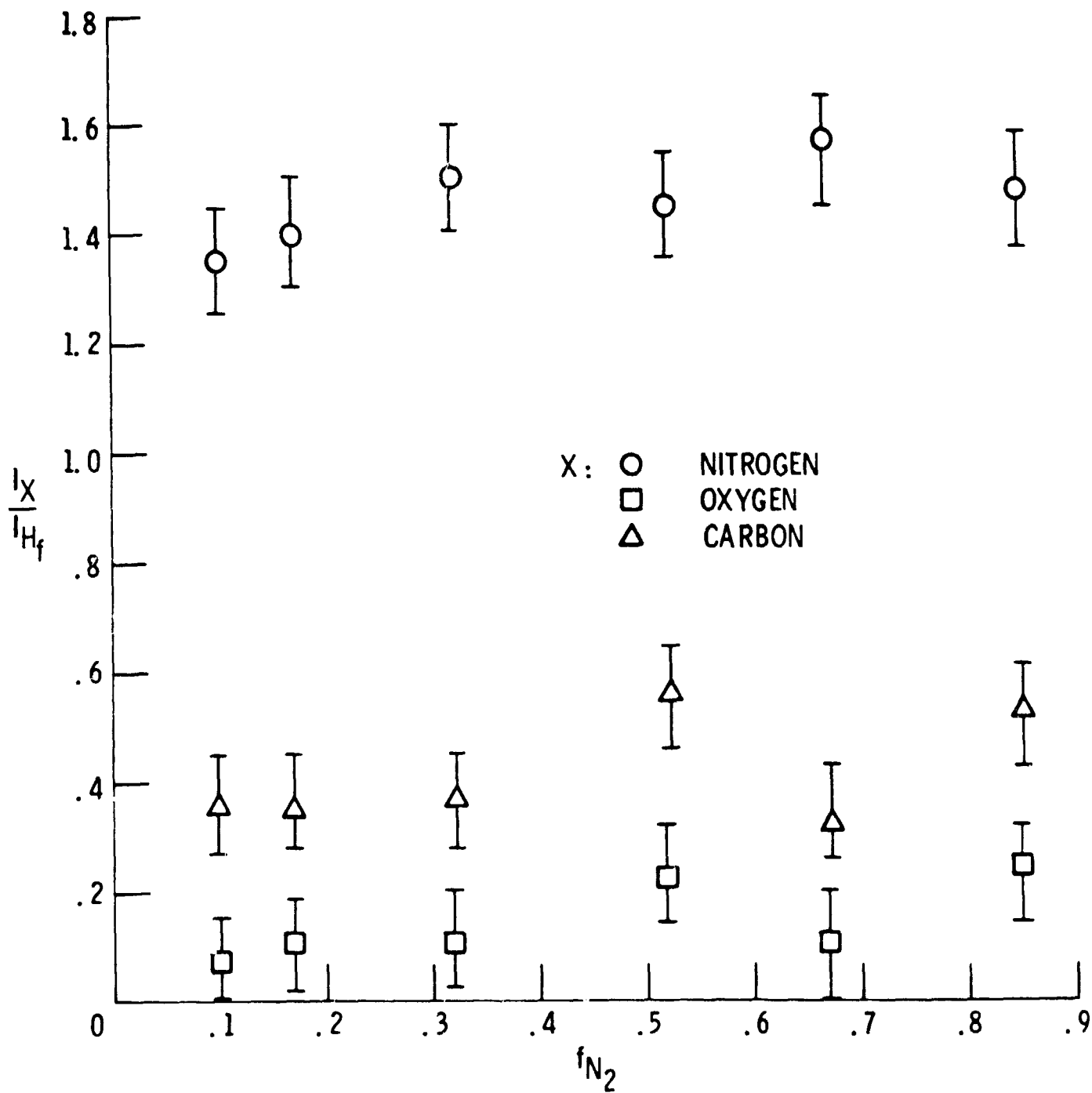
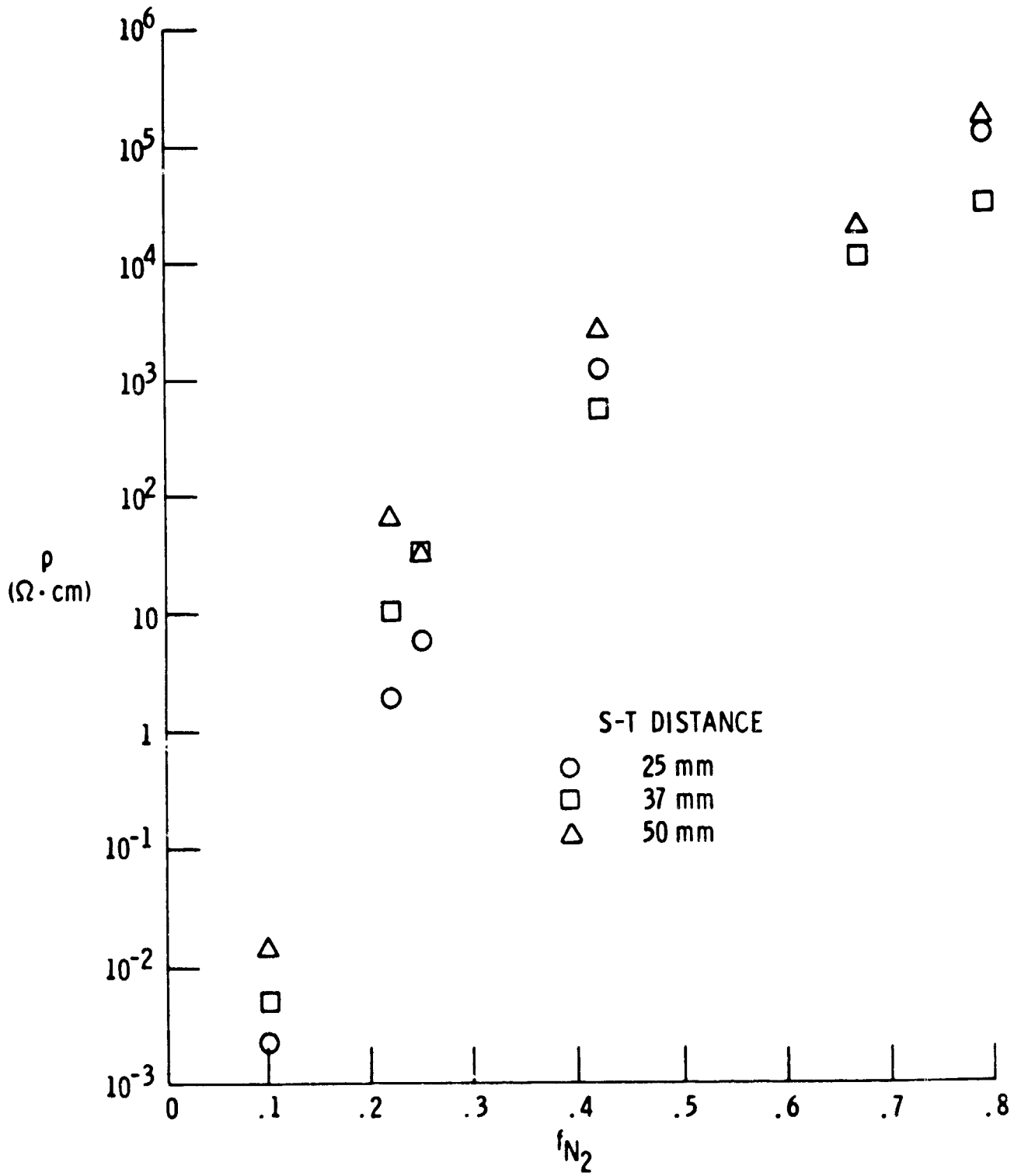Figure 2. - Ratios of AES peak heights to hafnium for nitrogen, oxygen and carbon as a function of f_{N_2}.

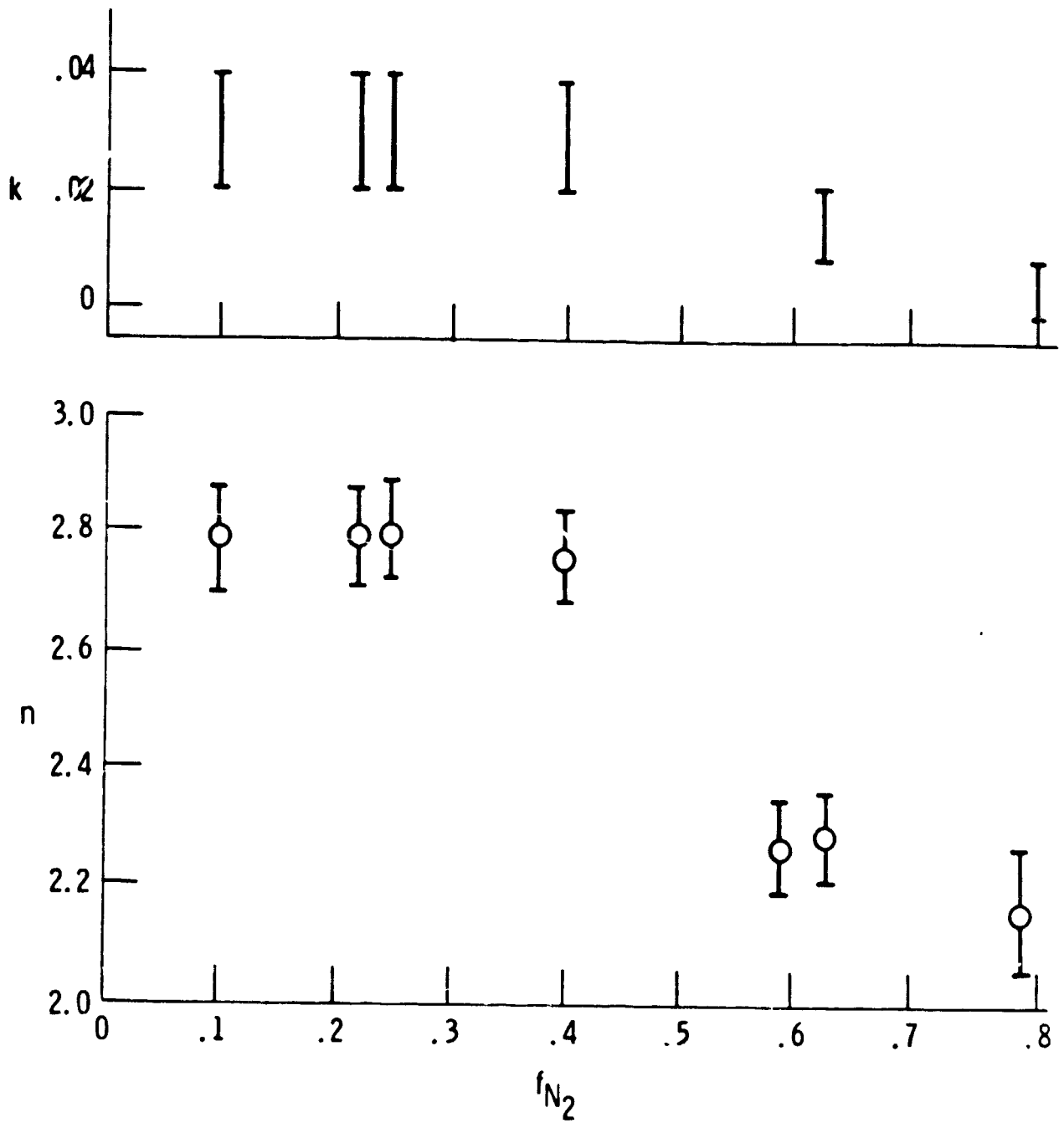Figure 3. – DC Resistivity as a function of f_{N_2} for 3 substrate to target distances.

Figure 4. - k and n as functions of f_{N_2}.