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Use of High L.E.T. Radiation to Improve Adhesion of Metals to Polytetrafluoroethylene

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Donald R. Wheeler and Stephen V. Pepper
Lewis Research Center
Cleveland, Ohio

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USE OF HIGH L.E.T. RADIATION TO IMPROVE ADHESION OF METALS TO POLYTETRAFLUOROETHYLENE

by Donald R. Wheeler and Stephen V. Pepper

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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ABSTRACT

We have used MgKα X-rays (1254 eV) and 2 keV electrons to irradiate the surface of PTFE. The damage is confined to a few tenths of a micron below the surface, and the doses exceed 10^8 rad. X-ray Photoelectron Spectroscopy (XPS) of the irradiated surfaces and mass spectroscopy of the gaseous products of irradiation indicate that the damaged layer is cross-linked or branched PTFE. After either type of irradiation, the surface has enhanced affinity for metals and a lower contact angle with hexadecane. Tape pull tests show that evaporated Ni and Au films adhere better to the irradiated surface. XPS shows that Ni interacts chemically with PTFE forming NiF_2 and possibly NiC. However, the gold adhesion and contact angle results indicate that the interaction is, at least in part, chemically non-specific. Decreased contact angles on FEP Teflon crystallized against gold have been attributed to either the presence of a polar oxygen layer or increased physical forces due to greater density. In the case of irradiated PTFE, we observe no oxygen on the surface. The cross-linked structure might, however, have a greater density, thus accounting for the observed increase in adhesion and wettability.

INTRODUCTION

In any surface analysis technique, the effect of the exciting radiation on the sample is a matter of concern. Polymers in general, and polytetrafluoroethylene (PTFE) in particular, are sensitive to radiation. Thus, study of the PTFE surface requires an awareness of the radiation effects to be expected. PTFE is known as a degrading rather than a cross-linking polymer, although cross-linking is possible (ref. 1). The usual decomposition mode is by chain scission followed by unzipping of the polymer. The product is almost 100 percent monomer. The same process is typical of thermal degradation (ref. 2). In a previous study (ref. 3), we have observed radiation damage to PTFE during X-ray photoelectron spectroscopy (XPS). The first part of the present report will review the nature of this damage as revealed by XPS of the PTFE surface and mass spectroscopy of the evolved gas. Subsequent observations on the similar effects of electron irradiation will also be presented.

The second part of this report will present some observations on the interaction of metals with both irradiated and unirradiated PTFE. The interaction of metals with polymers is of practical importance in metallization, tribology, and adhesive bonding. A common thread in discussions of polymer-metal interactions has been the role of chemical as opposed to physical forces. Chemical forces are produced by electron transfer between

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the metal and polymer, as occurs in conventional chemical bonding. Physical forces are produced by dynamic shifts in the electron density of one component in response to shifts in the other. These are also known as van der-Waals or dispersion forces, and are generally much weaker than chemical forces. The surface energy measured in wetting experiments is usually attributed to physical forces. Mittal has reviewed the various mechanisms of polymer-metal adhesion (ref. 4) and concludes that the physical force, or surface energy, is the most ubiquitous interaction. Important chemical forces do exist in polymer-metal systems, however. Burkstrand (ref. 5) has found a correlation between XPS evidence for chemical interaction and the strength of the polymer-metal bond.

In the case of fluoro-polymers, the situation is not clear. Shonhorn and Hara (ref. 6) have reported an increase in the surface energy of FEP Teflon crystallized against gold, but other investigators attribute this apparent surface energy effect to the chemical action of oxygen impurities at the interface (ref. 7). There is also XPS evidence for metal fluoride at the interface between FEP Teflon (ref. 8) and Al or Ti (but not Au) and between PTFE (ref. 9) and Ni.

In the present study, Ni and Au were evaporated onto both irradiated and unirradiated PTFE. Adhesion of the films was compared by a tape peel test, and the metal-PTFE interface was examined by XPS. Thin PTFE transfer films were applied to Ni, and those interfaces, too, were examined by XPS. Also, the contact angle of hexadecane was measured on both irradiated and unirradiated PTFE.

RADIATION DAMAGE

Polymer Structure

MgKα X-rays and 2 keV electrons were used in these experiments. Both have the property of producing unusually large radiation doses in the surface region of the PTFE sample. For example (ref. 10), the linear energy transfer (LET) of MgKα X-rays is greater than 15 keV/μm. The 1254 eV X-rays deposit all their energy in the first 0.1 μm of the sample, on the average. The corresponding dose rate is approximately 10^7 rad/s. This may be compared to typical radiation damage studies, in which the total dose may not exceed 10^8 rad (ref. 10). The extreme dose rates may account for the fact that the usual degradation of PTFE is not observed in these cases.

We have used XPS and mass spectrometry to study the effect of these high LET radiations on PTFE. Figure 1 shows the changes that occur in the C(1s) XPS spectrum of PTFE during irradiation. The features in the spectrum of the irradiated material are identified as components of a crosslinked or branched material. The same assignments have been made for plasma polymerized fluoro-carbons (ref. 11).

The mass spectrum of the gas evolved during irradiation is shown in table 1. For comparison the spectrum of the tetrafluoroethylene monomer and several saturated fluoro-carbons are also shown. Comparison of the spectra in the table shows that the evolved gas with major peaks at 69 and 31 amu consists of a variety of saturated fluoro-carbons. The monomer with major peaks at 31, 81 and 93 amu is not a significant part of the evolved gas.

On the basis of the C(1s) XPS spectrum, we propose that the incident radiation produces free fluorine radicals leaving chains with active sites trapped in the material. The active sites are known to be long lived

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(ref. 12), and as they accumulate under the very high dose used here, they are likely to find themselves able to form cross-linking bonds. In addition the radiation, either directly or through the free fluorine radical intermediaries, causes chain scission. Fluorine radicals and active chain sites are available to terminate these fragments so that unzipping need not occur. Thus the monomer which is the normal product of thermal degradation in vacuum is not observed in the mass spectrum. When one fragment of the chain is small enough and close enough to the surface it escapes into the gas phase and is detected by the mass spectrometer as a saturated fluoro-carbon.

Evidence of the same change appears in the C(1s) XPS spectrum when PTFE is irradiated with electrons except that the damage rate is much higher. The mass spectrum of the evolved gas is also the same in the case of electron irradiation.

Contact Angle

Measurements of the PTFE-hexadecane contact angle were made on both irradiated and unirradiated PTFE after they were removed from the vacuum system. The contact angle on unirradiated PTFE was 44°-45°, while it was 24°-30° on irradiated PTFE. It was thought that the change might be due to contamination of the irradiated surface on exposure to air. However, subsequent XPS analysis of specimens which had been exposed to air revealed no contaminants and no change in the structure of the C(1s) peak.

An effect, unrelated to surface forces, which could affect both contact angle and adhesion to irradiated PTFE is surface texturing. It has been observed (ref. 13) that ion beam irradiation of PTFE can produce a textured surface. Adhesion is improved on such a surface because of the increased surface area and mechanical interlocking. To rule out this possibility in the present experiments, scanning electron micrographs were made of the surfaces of both irradiated and unirradiated surfaces. Figure 2 shows the result. Although the magnification is more than sufficient to reveal structure on the scale reported in ion-beam texturing experiments, no difference in surface texture was discerned.

METAL-PTFE INTERACTION

Nickel Uptake

Samples of PTFE were coated with Ni by sublimation from a Ni filament located about 5 cm from the sample surface. The sublimation rate was such that a film thick enough to remove the C(1s) line from the XPS spectrum was formed after an exposure of 10 to 20 min. Film deposition was made in steps on both irradiated and unirradiated PTFE, and the Ni(2p3/2) XPS feature was recorded after each exposure. The area of the Ni(2p3/2) peak is a measure of the amount of Ni retained on the surface. It is shown as a function of exposure time in figure 3. From the initial slopes of the two sets of data, the uptake of Ni on the irradiated PTFE is almost twice that on the unirradiated PTFE. To achieve the maximum Ni(2p3/2) XPS intensity on the unirradiated PTFE requires about three times the Ni exposure that is required on the irradiated PTFE.

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Tape Peel Test

Nickel films were deposited onto irradiated and unirradiated PTFE, until the substrate could not be detected by XPS. The samples were then removed from the vacuum system and cellophane tape was pressed onto one-half of the specimen surface. It was then pulled free, the pull force being perpendicular to the sample surface. In every case of evaporation onto virgin PTFE, the nickel film was entirely removed by the tape test. In the case of irradiated PTFE, films were substantially intact after the test.

Gold films were deposited on irradiated and unirradiated PTFE substrates. The gold films were not as thick as the nickel films, since the C(1s) XPS peak was still detectable after evaporation. In cellophane tape peel tests such as those used on the nickel films, the gold films were removed entirely from both substrates. The same tests were then performed using tape with a much weaker adhesive. In that case the film on the irradiated PTFE was left intact while the film on unirradiated PTFE was partially removed. Finally, irradiated and unirradiated specimens of PTFE were transferred to another vacuum system and films of gold several thousand angstroms thick were evaporated onto them. Cellophane tape tests on these films showed patchy adhesion on the irradiated PTFE and no adhesion on the unirradiated PTFE.

These are qualitative tests and must be interpreted cautiously. However, we believe the results can be summarized in this way: Nickel films adhere better to irradiated than to unirradiated PTFE. Gold films also adhere better to irradiated than to unirradiated PTFE, but they never adhere as well as the nickel films on irradiated PTFE.

XPS Analysis of the Interface

The Ni-PTFE interface can be examined in two ways. A film of Ni can be applied to a PTFE substrate, or a film of PTFE can be applied to a Ni substrate. In either case, if the film is thin enough to permit the escape of a reasonable fraction of the photoelectrons, the interface will be accessible to XPS analysis. Evaporated Ni films on PTFE have been studied previously (ref. 14). The principal result is shown in figure 5. There is clear evidence for the formation of NiF_2 at the interface between Ni and X-ray damaged PTFE after evaporation. Furthermore, as Ni is deposited, the C(1s) peak showed a feature at low binding energy. This feature labeled P in figure 5 has not been identified with certainty, but seems to be an indication of interaction between the Ni and the polymer chain, itself.

Thin PTFE films were applied to sputter cleaned polycrystalline Ni by rubbing a PTFE sphere against Ni at low speed. It has been determined previously (ref. 15) that this process results in a transferred film of PTFE only a few monolayers thick, on the average. After application, the films were irradiated with 2kV electrons, and the Ni(2p3/2), F(1s) and C(1s) XPS peaks were monitored. Emission from the bulk of the Ni substrate will mask changes in the Ni XPS spectrum caused by changes at the interface, but, by the same token, changes in the PTFE spectrum should be dominated by the interfacial region.

Another difference between this and the work of reference 14 is that in this work, the main Ni(2p3/2) emission from the grounded Ni substrate can be used as a binding energy reference, provided the PTFE film is thin enough to be in good electrical contact with the Ni. Neither electron flood gun nor

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substrate bias revealed any charging. Therefore, in all remaining spectra, the Ni(2p3/2) peak is the binding energy reference.

The Ni(2p3/2), F(1s) and C(1s) peaks from the irradiated PTFE on Ni system are shown in figures 6 to 8, respectively. In each figure the spectra are shown before irradiation and after two different exposures to the 2 kV electrons. The Ni XPS spectrum in figure 6 confirms the previous observation of NiF_2 at the interface. The binding energies are more reliable here, because there was no charging. The reference peak positions are from reference 16. The production of fluoride is also evident from the F(1s) spectrum (fig. 7).

In both the F(1s) and C(1s) spectra, the main peak, which is presumably produced by atoms in the PTFE film, itself, is displaced to lower binding energy as the radiation dose increases, although the shoulder attributed to NiF_2 remains fixed. The shift does not appear to be a chemical shift since it is a gradual movement of the peaks rather than the growth of a peak at new binding energy. Furthermore, both the C(1s) and F(1s) peaks shift in the same direction by the same amount. A changed chemical interaction between carbon and fluorine atoms would produce shifts in opposite directions, and if the chemical interaction were with the nickel it is unlikely that carbon and fluorine with much different electronegativities would shift by the same amount, while the Ni(2p3/2) remained unchanged. The shift is in the wrong direction to be due to charging of the PTFE film, and attempts to detect charging using an electron flood gun and sample bias were all negative. Possibly, irradiation of the PTFE produces changes that permit greater relaxation of charge around the atom in which the core hole was produced by X-ray excitation of an atom. This will reduce the binding energy of the ejected electron by partially screening the core hole (ref. 17). In any event the magnitude of the effect varies with radiation dose and might shed light on the nature of the radiation damage, if it were better understood.

The effect of irradiation on the PTFE-Ni couple on the C(1s) peak is shown in figure 8. The features labeled P_2 and P_3 are the effects of irradiation on bulk PTFE that were noted before (ref. 3). As the radiation dose increases, these features shift to lower binding energy along with the main peak. That is to be expected, because of screening, if the peaks are produced by atoms in the film, rather than at the interface. There is no evidence for the feature associated with deposition of Ni on PTFE which should occur at P in the figure. If this feature is an interfacial feature, like the low binding energy feature in the F(1s) spectrum, it should not shift to lower binding energy as the dose increases, because the interfacial atoms are coupled to the substrate Fermi level. Thus, if P is present, it may well be obscured by the radiation damage structure in the C(1s) peak as it shifts to lower binding energy.

CONCLUSIONS

Four distinct observations have been made, here. First, XPS and mass spectroscopy show that irradiation of PTFE with high LET radiation produces a heavily branched and/or cross-linked surface region. Second, this modified surface is a higher energy surface than the unirradiated one as shown by the decreased hexadecane contact angle. Oxygen is not likely to contribute to the effect in this case. Third, the XPS spectra of the metal-PTFE interface indicate that at the interface between the irradiated PTFE surface

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and Ni there is Ni fluoride and possibly a Ni-carbon chemical interaction. Neither fluorides nor carbon interaction are observed at the gold-PTFE interface, however. Finally, both Ni and gold films adhere better to the irradiated than to the unirradiated surface, as shown by the tape peel tests, with Ni adhering better than gold.

Several conclusions may be drawn. First, increased physical forces at the irradiated PTFE surface make a significant contribution to the improved metal adhesion on irradiated PTFE. If this were not the case, it would be very difficult to explain the improved adhesion of the chemically inactive gold films. Increased density of the cross-linked polymer may explain the increase in surface energy.

Second, the fluoride that forms at the interface correlates directly with radiation dose. Fluorides observed previously at normally unirradiated PTFE-metal interfaces (refs. 8 and 9) are likely to be artifacts of the irradiation used in analysis. Fluorine free radicals migrating to the PTFE surface would normally escape. If a metal is present, however, they are trapped as fluorides which accumulate at the interface.

Finally, the fact that Ni adheres better than gold to irradiated PTFE, suggests that chemical forces as well as physical forces may be important. It is hard to see how the fluoride can be responsible for improved adhesion, but the C(1s) feature at low binding energy which is seen in figure 5 may be due to an interaction between Ni and the polymer chain itself. In any case the oxygen observed in reference 7 is absent in these experiments.

Quantitative correlation between the degree of chemical change evident in the XPS spectrum and the increase in adhesion would do much to clarify the different roles of physical and chemical forces. The progressive and controlled change in adhesion that can be produced by irradiation of PTFE should prove most useful in the development of quantitative adhesion measurements.

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TABLE I. - MASS SPECTRA OF IRRADIATED PTFE AND SOME FLUOROCARBON GASES ALL SPECTRA NORMALIZED TO LARGEST PEAK

M/e	Species	Irradiated PTFE	C_2F_4 (100 amu)	CF_4 (88 amu)	C_2F_6 (138 amu)	C_3F_8 (188 amu)	C_4F_{10} (238 amu)
12	C	4.3	6.6	13.0	5.0	<1	1.9
19	F	2.5	3.2	9.8	6.7	0	1.1
24	C_2	0	2.6	0	0	0	0
31	CF	23	100	9.8	55	28	20
50	CF_2	7.5	22	16	17	6.1	3.4
62	C_2F_2	0	1.0	0	0	0	.32
69	CF_3	100	2.7	100	100	100	100
81	C_2F_3	.57	28		0	0	.38
93	C_3F_3	.94	14		0	.24	.57
100	C_2F_4	3.2	0		0.33	2.4	3.2
119	C_2F_5	7.2			20	2.5	6.0
131	C_3F_5	2.3				.04	3.0
150	C_3F_6	.023				0	.47
169	C_3F_7	1.1				1.6	.20
181	C_4F_7	.18					0
219	C_4F_9	.085					.15
231	C_5F_9	.023					
269	C_5F_{11}	.0094					
281	C_6F_{11}	.0038					

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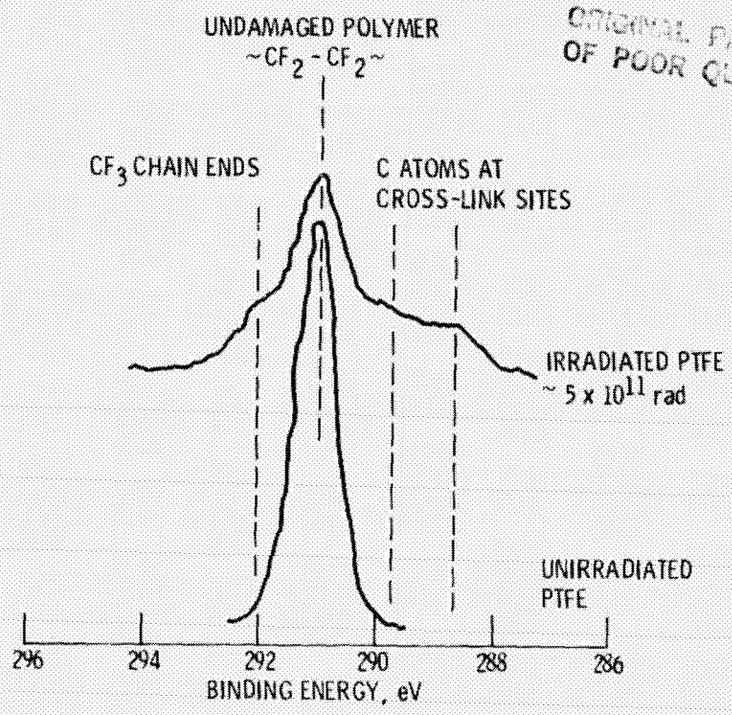

Figure 1. - Effect of irradiation on PTFE structure as shown in XPS C (1s) peak.

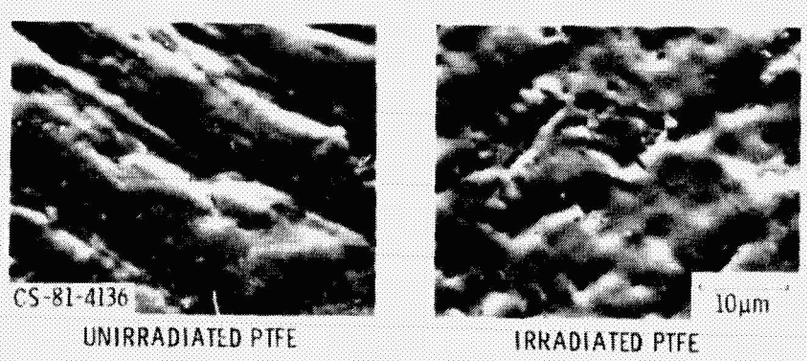

Figure 2. - Scanning electron micrograph of irradiated and unirradiated PTFE Mg Kα radiation, 24 hr exposure.

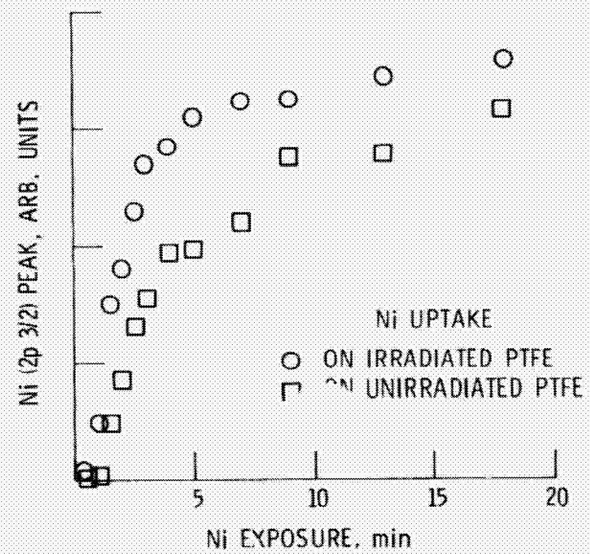

Figure 3. - Ni(2p 3/2) XPS peak height versus time of exposure to Ni filament for both irradiated and unirradiated PTFE substrates.

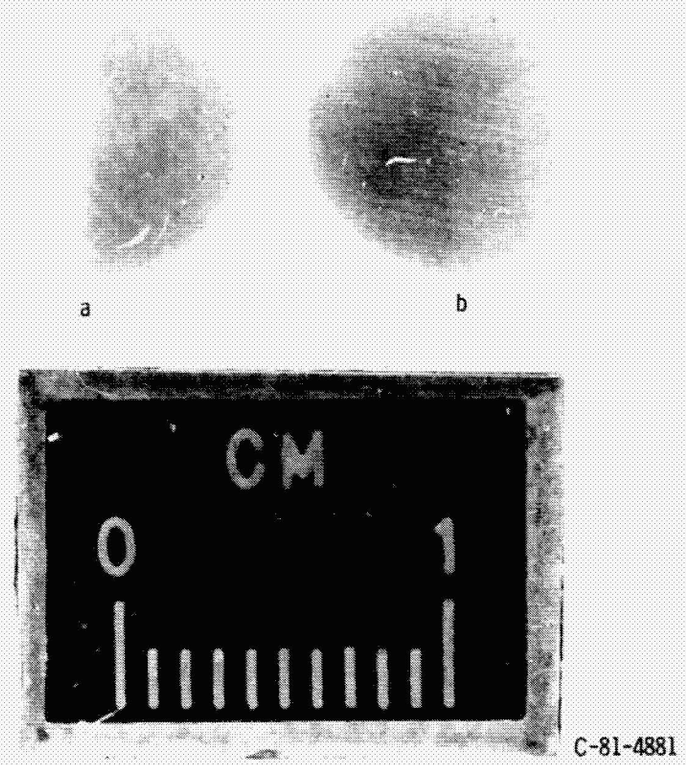

Figure 4. - Results of tape peel tests on (a) unirradiated and (b) irradiated PTFE

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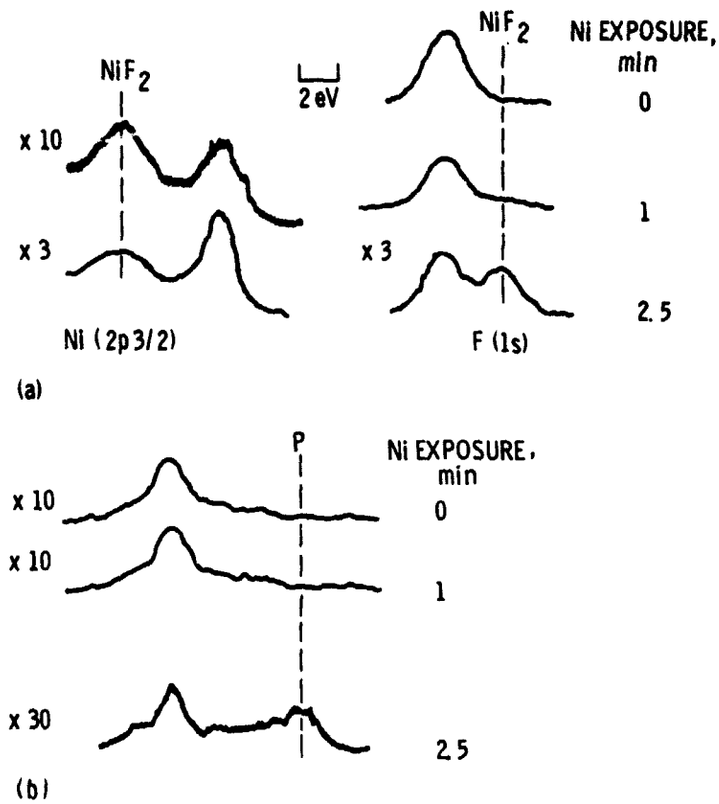

(a) Ni (2p3/2) and F (1s) XPS peaks showing growth of fluoride after Ni deposition.

(b) C (1s) XPS peak showing growth of low binding energy feature "P" after Ni deposition.

Figure 5. - XPS features from irradiated PTFE before and after deposition of Ni.

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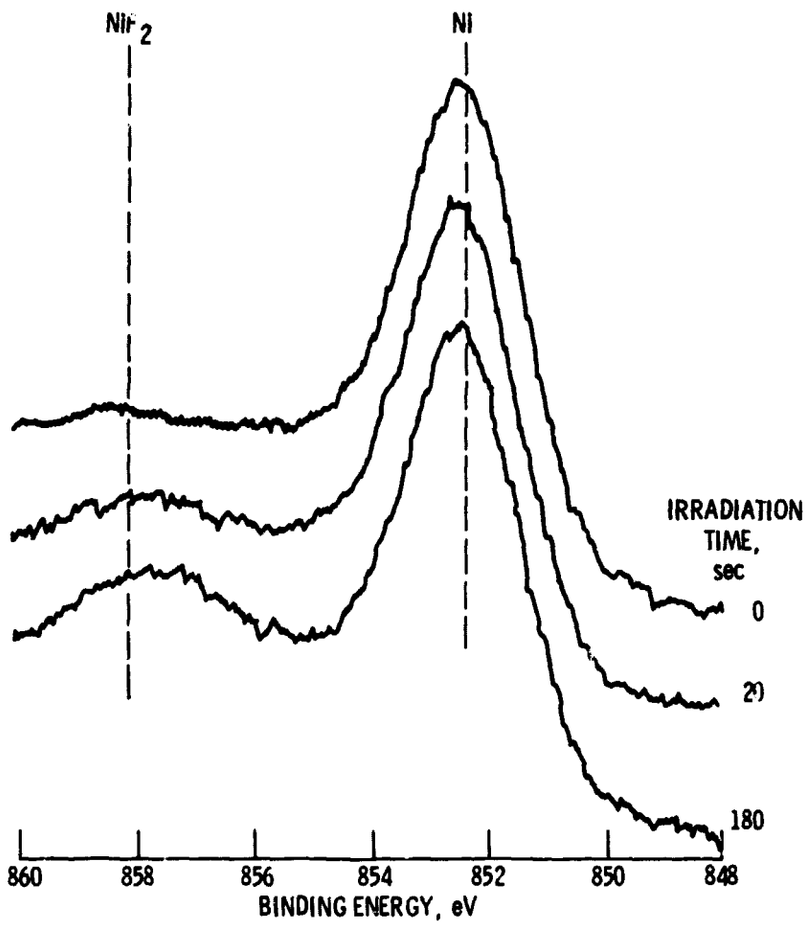

Figure 6. - Ni (2p 3/2) peak from polycrystalline Ni with PTFE transfer film, showing increase in NiF_2 with electron irradiation, 2 kV, 2.4 μA.

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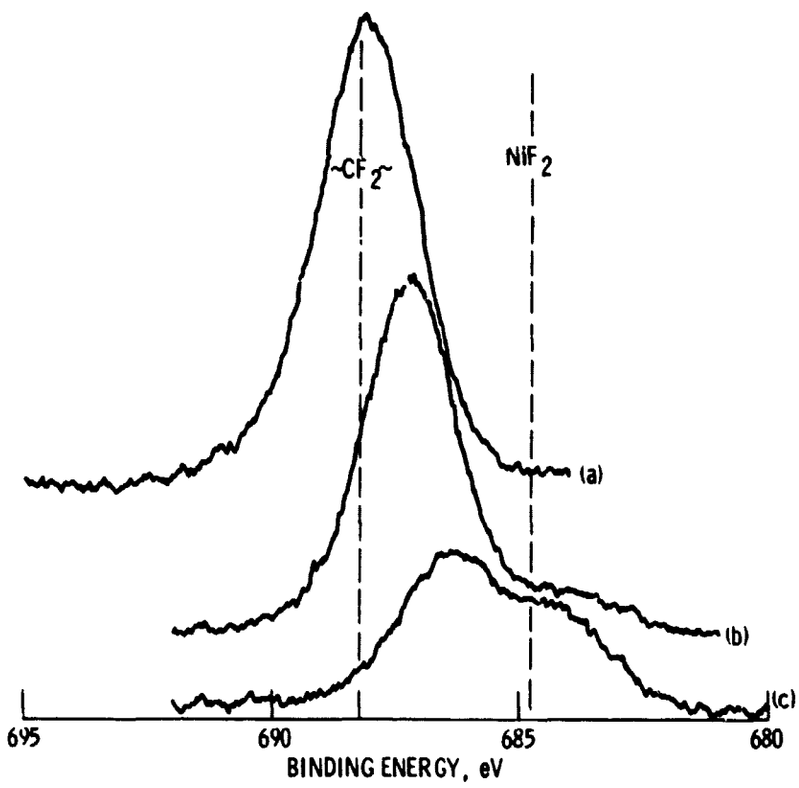

Figure 7. - F(1s) XPS peak from PTFE transfer film on Ni irradiated with 2 kV electrons, 2.4 μA for (a) 0 sec; (b) 20 sec; (c) 180 sec; showing increase on NiF_2 with irradiation.

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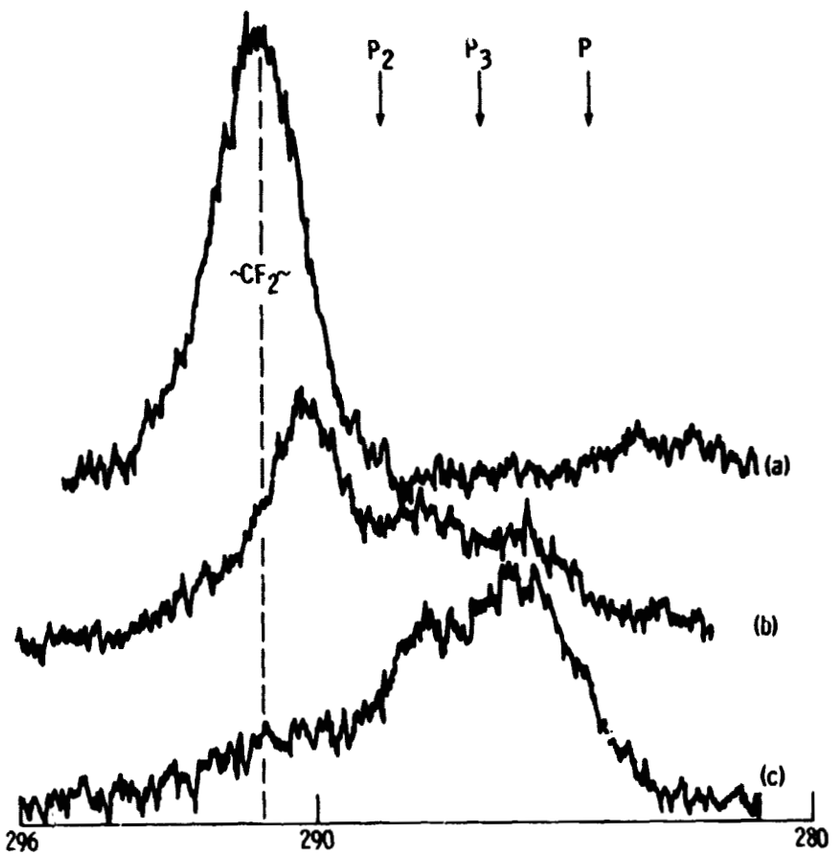

Figure 8. - C(1s) XPS peak from PTFE transfer film on Ni irradiated with 2 kV electrons, 2.4 μA for (a) 0 sec; (b) 20 sec; (c) 180 sec location of features P_2 and P_3 from ref. 3 and feature P from ref. 14 shown.